AN INTRODUCTION TO MODERN THERMODYNAMICAL PRINCIPLES

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INTRODUCTION

THE primary object of thermodynamics is to describe the behaviour of systems in equilibrium, in such a way that this behaviour is known quantitatively when equilibrium conditions such as temperature and pressure are altered. Using the first and second laws of thermodynamics, it is possible to define certain functions, such as the entropy and free energy of the system, which give a formal description of the behaviour of the system in a very elegant way. Thermodynamics is, however, essentially a practical science. The chief progress in the last thirty years has been in devising methods of evaluating thermodynamic functions rather than in extending their formal applications. From a practical point of view the problem is always to express the thermodynamic functions in terms of quantities which are more easily observed experimentally. Such progress has been made that the historic method of deriving the law of mass action from the theory of the velocity of reactions, and the concept of dynamic equilibrium, has been inverted. One of the tentative applications of thermodynamic functions at the present time is in the calculation of reaction velocity.

The aim of the present book is to describe briefly the formal applications of thermodynamic functions to the calculation of physico-chemical equilibria. This is followed by a description of the experimental methods of evaluation that are available. Direct measurements on equilibrium processes have been very fully described elsewhere (e.g. Lewis and Randall, *Thermodynamics*, McGraw Hill Co., 1923), so that attention is principally paid to the fundamental departure of evaluating entropy and free energy from the heat content, which is much more easily measured. This involves a careful discussion of the Nernst Heat Theorem.

Such a discussion is not possible without at least an elementary treatment of statistical theory. The relation between the thermodynamic functions and the partition function (*Zustandsumme*) is therefore discussed in an elementary way, the aim being to give a sufficiently complete account for thermodynamical requirements without assuming the burdens of a more detailed statistical theory.

The theory of the partition function is also required for the recently developed methods of calculating thermodynamic functions from spectroscopic data. Here again an attempt has been made to discuss the principal methods used, so as to give an account which is fairly complete from the thermodynamical aspect, without going too far into difficulties which merely arise from complications in certain band spectra.

The application of velocity considerations to the calculation of equilibria, as in the adsorption of gases, is also briefly described, in order to complete the list of subjects which are not always treated very adequately in ordinary text-books on thermodynamics. For the converse reason, practically no reference is made to the subject of electrolytes.

The book is based on lectures delivered in the Department of Thermodynamics in Oxford.

THE USE OF THERMODYNAMIC FUNCTIONS

THERMODYNAMICS deals primarily with systems in equilibrium. It aims at describing completely the behaviour of all imaginable systems in equilibrium, when various factors such as temperature, pressure, and concentration of the various components are altered. With ninety-two elements and the innumerable compounds which can be obtained from them the number of imaginable systems is, however, very large. Even if only those of practical importance had each to be investigated experimentally before anything could be said of them, the prospect would be rather dismal.

Fortunately, thermodynamics provides a number of theoretical propositions which enormously simplify the problem. One of these is the Phase Rule, which states that the number of undetermined variables, or degrees of freedom, F, is not arbitrary, but is given by the rule $F = C-P+2$, where C is the minimum number of components required to describe each phase of the system completely, and P is the number of phases.

A second way in which the study of systems in equilibrium can be greatly simplified is by the use of thermodynamic functions, which are based on the first and second laws of thermodynamics, and which can be evaluated for each single substance separately. As is explained in what follows, the thermodynamic functions of the substances A, B, C permit the evaluation of the functions for any system composed of them, without further experiment, so that it is possible in principle to calculate the position of equilibrium in all combinations of A, B, C taken two or more at a time, and thus to cover $n!$ systems (apart from limitations of valency) with only n determinations. Although the calculation of thermodynamic functions offers both theoretical and experi-

mental difficulties, their very practical use, once they are determined, is clear. Practically all the progress in modern thermodynamics depends on the development of convenient methods for determining the thermodynamic functions of individual substances.

Thermodynamic functions based on the first law

The heat content $\mathfrak{H}$ and the internal energy E.

Two important properties of all thermodynamic functions may be illustrated from one of the simplest, the heat content $\mathfrak{H}$. If two different states of a single substance or a system can be characterized by different values of temperature, pressure, concentrations, etc., the increase in heat content of a system in changing from state A to state B is defined as the energy taken up when the change is carried out at constant pressure. The symbol i and the name Enthalpy have also been used for this function.

Acquisitive convention as to signs.

It should be noted at the outset that various conventions as to whether a change in heat content is to be counted negative or positive have been used, according to the preferences and nationality of the author. This variability leads to confusion. By analogy with the universal nature of human acquisitiveness, which transcends national boundaries, when a system gains in entropy, energy, etc., the change will be accounted as positive. In the same way mass action constants are written with the products in the numerator. The definition of the change in heat content may be symbolized by the equation $\Delta\mathfrak{H} = \mathfrak{H}_b - \mathfrak{H}_a$, where $\mathfrak{H}_a$ and $\mathfrak{H}_b$ are the heat contents in the states A and B. The first important property of the function $\mathfrak{H}$ is that the value of $\Delta\mathfrak{H}$ depends only on the initial and final states of the single substance or system under discussion, and not on the process by which the change is brought about.

This property follows from the first law of thermodynamics, which states that energy can neither be created nor destroyed. If it were possible to have two different processes with different changes in heat content in going from A to B, it would be possible by working one of the processes in the opposite direction to set up a cycle, leading to the indefinite production or destruction of energy without permanent change in the working substance. This is contrary to the first law. The value of the function $\mathfrak{H}$ in any state is thus dependent only on what that state is, and not on previous history.

In the language of the differential calculus, this property, which is common to all thermodynamic functions, though for different reasons, is expressed by the statement that $d\mathfrak{H}, dS$, etc., are complete differentials, i.e. that in any small change in the system, which can be expressed in terms of changes in the variables x_1, x_2, x_3,... characterizing it, the change $d\mathfrak{H}$ is not arbitrary, nor dependent on previous history, but is given completely by the expression

$$d\mathfrak{H} = \left(\frac{\partial \mathfrak{H}_1}{\partial x_1}\right) dx_1 + \left(\frac{\partial \mathfrak{H}_2}{\partial x_2}\right) dx_2 + \left(\frac{\partial \mathfrak{H}_3}{\partial x_3}\right) dx_2 + \dots .$$

A second important property of the heat content, and of other thermodynamic quantities such as the volume, the entropy, etc., is that they are extensive, i.e. that the numerical value is directly proportional to the mass of working substance taken. This follows from the fact that the change in heat content in any process is the same if the substance as a whole is brought from state A to state B, or if it is first subdivided (which does not require any work) and the individual portions are brought from state A to state B separately. This property may be symbolized by the equation $\mathfrak{H} = nH$, where H is the heat content per mole, and there are n moles in the mass of working substance chosen. Extensive properties should be contrasted with intensive properties

such as temperature and pressure, which must be the same throughout a system in equilibrium and do not depend on the quantity of working substance.

Hess's law.

From these two properties it follows that the heat content per mole may be treated like any other quantity in a chemical equation. Thus from the equations

$$CaCO_3 \rightarrow CaO + CO_2 \quad + \Delta H_1,$$
$$C + CO_2 \rightarrow 2CO \quad\quad + \Delta H_2$$
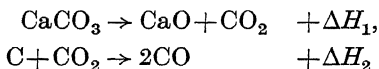
it follows by direct addition that the change in heat content in the reaction

$$CaCO_3 + C \rightarrow CaO + 2CO \quad + \Delta H_3$$
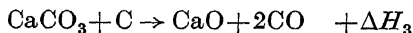
is simply $\quad\quad \Delta H_3 = \Delta H_1 + \Delta H_2.$

Hess's law is of great value in thermochemistry for the calculation of changes in heat content which cannot be obtained by direct calorimetry. Since all the other functions to be defined possess the same two properties as the heat content, one means of calculating thermodynamic quantities not directly accessible to experiment is evidently to combine two or more equations for which they can be estimated.

Measurements of heat content; choice of a reference state.

The *change* in heat content in a large number of processes can be measured quite conveniently in suitable forms of calorimeters, as well as by other means such as spectroscopic observations. The heat content in any single state is to some extent arbitrary, since only differences in heat content can be measured. Any one state of a substance or system may therefore be selected as reference state, and the heat content of all other states referred to the selected state as zero. When a suitable reference state has been chosen the change in heat content in passing to any other state A may be written in full

$$\Delta H_a = H_a - H_{standard}.$$

Where no ambiguity can arise the symbol H_a is simply used for the heat content in the state A, referred to the standard state as zero.

The particular state chosen as zero makes no difference to the change in heat content in proceeding from one state A to another B, since the difference

$$\Delta H_{a,b} = (H_b - H_{\text{standard}}) - (H_a - H_{\text{standard}})$$

is independent of what value is chosen as standard. The choice of a suitable zero state for thermodynamic functions is, however, important when these are to be correlated with statistical theory, and is referred to again below. A further practical consideration in the choice is that the changes can be accurately measured, i.e. that the standard state is experimentally accessible.

The internal energy E.

When a system passes from state A to state B at constant volume the increase in internal energy is defined as

$$\Delta E = E_b - E_a,$$

the net energy absorbed. Just as with the heat content, the values of E_b and E_a are to some extent arbitrary, and the internal energy of a system in any state must be referred to a suitable reference state, from which the differences can be measured. From the first law of thermodynamics, the increase in heat content in any process must be equal to the increase in internal energy + the work done on the system by the external pressure. The relation between the two functions can thus be written

$$\Delta H = \Delta E + P(V_b - V_a)$$

or

$$H = E + PV.$$

In general, thermodynamic functions referring to changes at constant pressure are more convenient for experimental determination, whereas functions referring to constant volume are more suitable for theoretical calculation. The

relations between the different functions, which are used for calculating one from another, are discussed below.

Thermodynamic functions based on the second law

For calculating the equilibria among chemical substances it is necessary to use functions based on the second law as
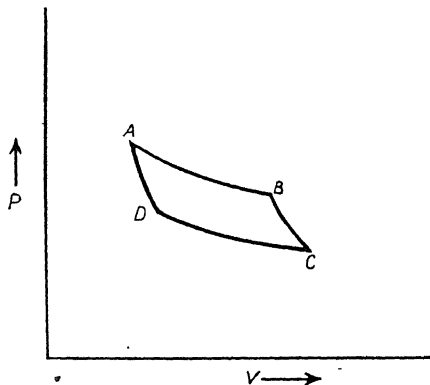

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well as the first. The simplest of these is the entropy S. The increase in entropy of a system in any change is defined as $\Delta S = Q/T$, where Q is the heat absorbed and T is the absolute temperature, provided the change is reversible. This provision is made to preserve the essential property that the entropy difference between any state and a standard reference state shall depend only on that state, and not on the previous history of the working substance, i.e. that dS shall be a complete differential. As a result of the condition of reversibility the quantity $T\Delta S$ for a change from a state A to a state B is in general quite different from the calorimetric heat of reaction, which would be observed when the change is carried out under irreversible conditions.

The way in which this property depends on the second law of thermodynamics may be seen from a simple Carnot's cycle.

AB, CD are isothermals, BC and AD adiabatics. The entropy change in proceeding from A to B is

$$\Delta S = S_B - S_A = \frac{Q_{AB}}{T_1}.$$

From B to C there is no entropy change. From C to D the change is

$$\Delta S = S_D - S_C = \frac{Q_{CD}}{T_2}.$$

From D to A there is no entropy change.

From the second law of thermodynamics, if the process is carried out reversibly in every part,

$$\frac{Q_{AB}}{T_1} = \frac{Q_{CD}}{T_2},$$

i.e. $$S_B - S_A = S_D - S_C.$$

Provided the heat absorbed is measured in any other reversible change,

$$\int_A^B \frac{dQ}{T} = S_B - S_A$$

must still be the same. If this were not the case, it would be possible to construct a cycle for converting the heat of the surroundings indefinitely into work, contradicting the second law. It follows that the entropy change can depend only on the initial and final states, and not on the (reversible) path. This is the property required.

Like the heat content and internal energy, S is an extensive property whose value is proportional to the working mass of the substance, so that entropy changes can be included as one of the terms of a chemical equation. Unlike the heat content, however, whenever the change has to be measured experimentally care must be taken that the process chosen is reversible at every stage.

All the other thermodynamic functions used are derived from these three, and consequently share the same properties of depending only on the actual state of the substance (and

the reference state), and of being extensive. The most used
are:

The Free Energy: for processes occurring at constant pressure.

This is defined as $F = H - TS$, and was called the thermodynamic potential by Gibbs.

The Available Energy: for processes occurring at constant
volume.

This is defined as $A = E - TS$ and has occasionally been
termed the free energy by older writers on thermodynamics.

Planck's Thermodynamic Potential ϕ.

This is simply defined as $\phi = F/T$ and has certain formal
advantages in some thermodynamic equations.

Owing to the fact that these functions have been differently
named by various authors, it is convenient to remember
that the quantity F measures the total energy intake H
minus the heat $T\Delta S$ absorbed in a reversible process occurring
at constant pressure. The net energy 'freed' in the process
and available for mechanical work is thus $-F$. Similarly,
the quantity $-A$ is the net energy 'available' for mechanical
work in a reversible process at constant volume.

THERMODYNAMIC RELATIONSHIPS

BEFORE discussing the problem of physicochemical equilibrium it is useful to consider the minimum number of variables such as pressure, temperature, concentrations of the various components, etc., required to define completely any system. Qualitatively the problem is solved by the Phase Rule, symbolized as $F = C - P + 2$, where C is the minimum number of molecular components required to describe the composition of every phase, P is the number of phases, and F is the number of degrees of freedom, i.e. the number of variables which can be altered *independently* without causing disappearance of one of the phases.

The quantitative treatment depends on certain relationships between the thermodynamic functions, and other variables such as temperature and pressure. It is particularly important to summarize such relationships as are used for calculating the values of thermodynamic functions from quantities which are more accessible to experiment.

The heat content and the internal energy.

For these two functions, by definition

$$= C_P \qquad H_{T_1} - H_{T_2} = \int_{T_2}^{T_1} C_P \, dT,$$

$$\frac{\partial E}{\partial T}\Big)_V = C_V \qquad E_{T_1} - E_{T_2} = \int_{T_2}^{T_1} C_V \, dT,$$

where C_P and C_V are the molar specific heats at constant pressure and constant volume respectively.

The magnitude of H_{T_1} and E_{T_1} relative to suitable reference states T_2 can thus be determined by integrating the plot of specific heat against temperature, usually graphically. Since extrapolation to absolute zero (cf. p. 13) is quite

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reliable for C_V, it is possible in many cases to use the heat contents at absolute zero as standards of reference for the individual substances taking part in a reaction. This has the further advantage that the heat of reaction at absolute zero can be directly related to linking energies of chemical bonds.

Since specific-heat measurements are primarily carried out at constant pressure, the values of H are much easier to evaluate than values of E, particularly for solids and liquids. The values of C_V and E are, however, of particular importance for the theory of the solid state (cf. p. 61). Various transformation formulae between the two functions have to be used in calculating E from H. These can be derived as follows:

At constant pressure $H = E + PV$ and

$$\left(\frac{\partial H}{\partial T}\right)_P dT = \left(\frac{\partial E}{\partial T}\right)_P dT + P\,dV,$$

i.e.

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right) \qquad (1)$$

Also, since E is a function of T and V,

$$dE \quad \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV,$$

e.

$$\left(\frac{\partial E}{\partial T}\right)_P = \quad + \quad {}_T\left(\frac{\partial V}{\partial T}\right)_P$$

$$= C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P. \qquad (2)$$

Combining formulae (1) and (2):

$$C_P - C_v \quad \left(\frac{\partial V}{\partial T}\right)_P \left\{ P + \left(\frac{\partial E}{\partial V}\right)_T \right\}.$$

For purposes of calculation this expression still has the disadvantage that $(\partial E/\partial V)_T$ is not usually available, unless the equation of state is known experimentally. For a perfect gas this term is of course zero. A further transformation can

be obtained by using the entropy function, i.e. by introducing the second law of thermodynamics.

Thus in any reversible change $dE = T\,dS - P\,dV$,

i.e.
$$\frac{\partial E}{\partial V}\bigg)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

and
$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial V}\right)_T.$$

Also
$$\frac{\partial S}{\partial V}\bigg)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{(see equation (1), p. 14),}$$

so that
$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V. \tag{1}$$

Still another transformation follows from the fact that P is a function of V and T so that

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV,$$

or at constant pressure

$$0 = \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P. \tag{2}$$

Eliminating $(\partial P/\partial T)_V$ from (1) and (2), since it is a quantity difficult to determine experimentally for condensed phases (solids and liquids),

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2,$$

or since the compressibility

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

and the cubical coefficient of expansion

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \qquad C_P - C_V = \frac{\beta^2 V}{K}\,T.$$

This formula is occasionally written with the linear coefficient of expansion $\alpha = \beta/3$, in which case

$$C_P - C_V = \frac{9\alpha^2 V}{K}\,T.$$

The object of these formulae is in every case to calculate important quantities from results which are fairly readily obtained experimentally. When even the compressibility is not known, e.g. at low temperatures, it is possible to use empirical formulae such as

$$C_P - C_V = A T^{\frac{3}{2}} \quad \text{or} \quad \frac{C_P}{C_V} = 1 + \frac{A C_V}{T}$$

where the constant A has in each case to be evaluated at a temperature where C_P and C_V are both known.

Other relationships between H or E and the different variables available may be readily derived (cf. p. 16) but are seldom used experimentally.

The entropy S

The exact evaluation of the entropies of chemical compounds has been greatly developed in recent years, owing to its importance in the calculation of equilibria.

By definition, if dQ is the heat absorbed in a reversible change, the increase in entropy of the system

$$dS = \frac{dQ}{T}.$$

Thus

$$(dS)_P = \frac{C_P dT}{T}$$

and

$$(S_{T_1} - S_{T_2})_P = \int \frac{C_P dT}{T} = \int_{T_2}^{T_1} C_P \, d \ln T.$$

Similarly,

$$(S_{T_1} - S_{T_2})_V = \int_{T_2}^{T_1} C_V \, d \ln T.$$

For the calculation of entropies the reference state is usually chosen to be the crystalline solid at absolute zero, since this choice has important theoretical advantages (cf. p. 27). From the practical standpoint, however, it should be noted that many solids have specific heat anomalies at low

temperatures. The contribution of such anomalies to the heat content, in a graphical evaluation of the integral

$$\int\limits_{\cdot}^{\cdot} C_P \, dT = H,$$

is insignificant, of the order of a few calories, but their contribution to the entropy cannot be neglected. In the plot of C_P against $\ln T$, which is used in a graphical evaluation of the entropy, it is not the magnitude of dQ but of dQ/T which is relevant, so that quite small heat changes make important contributions to the entropy when the temperature at which they occur is sufficiently low. These specific-heat anomalies are discussed in more detail below.

Important relationships between entropy and other variables may be summarized:

(a) *Dependence on volume and pressure.* In an infinitesimal reversible change the increase in internal energy dE is equal to the heat absorbed minus the external work done by the system; i.e.

$$dE = T \, dS - P \, dV,$$

or
$$P = T \left(\frac{\partial S}{\partial V} \right)_T - \left(\frac{\partial E}{\partial V} \right)_T. \tag{A}$$

Similarly, using the relation
$$dH = dE + P \, dV + V \, dP$$
$$= T \, dS + V \, dP,$$
$$V = -T \left(\frac{\partial S}{\partial P} \right)_T + \left(\frac{\partial H}{\partial P} \right)_T. \tag{B}$$

Differentiating (A) with respect to T at constant volume,

$$\left(\frac{\partial P}{\partial T} \right)_V = T \, \frac{\partial^2 S}{\partial T \partial V} + \left(\frac{\partial S}{\partial V} \right)_T - \frac{\partial^2 E}{\partial T \partial V},$$

and since
$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_V = \frac{C_V}{T},$$

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{1}{T} \left(\frac{\partial C_V}{\partial V} \right)_T = \frac{1}{T} \, \frac{\partial^2 E}{\partial T \partial V},$$

so that the second and fourth terms cancel.

Thus
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \tag{1}$$

and equation (A) transforms to the 'thermodynamic' equation of state of a substance:

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T. \tag{A'}$$

Similarly, using the heat-content equation (B),

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \tag{2}$$

and the second 'thermodynamic' equation of state is

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T. \tag{B'}$$

These theoretically exact equations of state are useful checks on empirical equations, e.g. in calculating the Joule-Thomson effect $(\partial H/\partial P)_T$ in terms of the equation of state. They are inserted here since they also permit thermodynamic functions to be evaluated when the equation of state is known. For a perfect gas, for example, the equation of state is $PV = RT$,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\frac{R}{P};$$

also $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} = \frac{5R}{2T}$ for a perfect monatomic gas.

Thus
$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$$
$$= -\frac{R}{P}dP + \frac{5R}{2}\frac{dT}{T},$$
$$S = R\ln\frac{T^{\frac{5}{2}}}{P} + \ln A,$$

where A is a constant (the entropy constant of a perfect monatomic gas) whose evaluation requires statistical mechanics, and is discussed later (cf. p. 96). For a perfect diatomic gas the entropy due to the translational specific

heat has the same value, but terms have to be added for the vibrational and rotational specific heats, since these also occur in the integral

$$S = \int C_P\, d \ln T.$$

The problem is further discussed on p. 100.

The free energy and the available energy

These functions are defined by the equations

$$F = H - TS$$

and
$$A = E - TS$$

and are more convenient than the entropy in dealing with problems of chemical equilibrium.

Differentiating,

$$\left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T \tag{1}$$

$$= V \quad \text{(cf. equation (B'), p. 14)} \tag{2}$$

and
$$\left(\frac{\partial F}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_P - S \tag{3}$$

$$= -S$$

$$= \frac{F - H}{T}. \tag{4}$$

Similarly,

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{(using equation (A'), p. 14)} \tag{5}$$

and
$$\left(\frac{\partial A}{\partial T}\right)_V = -S = \frac{A - E}{T}. \tag{6}$$

Equations (4) and (6) are known as the Gibbs-Helmholtz equations, and are of great importance experimentally in calculating the variations of F and A with temperature.

Equations (2) and (5) may be used for calculating the values of F and A from equations of state, e.g. for an

imperfect gas. For a perfect gas, whose equation of state is $PV = RT$,

$$(dF)_T = \frac{RT}{P}\, dP,$$

$$F_1 - F_2 = RT \ln P_1/P_2$$
$$= RT \ln C_1/C_2,$$

where C_1 and C_2 are concentrations expressed in suitable units. Similarly,

$$A_1 - A_2 = RT \ln V_2/V_1 = RT \ln P_1/P_2.$$

Both these changes refer to processes carried out at constant temperature.

Thermodynamic functions and other variables

Since each of the thermodynamic functions refers only to the actual state of the system, and not to its past history, each is a complete differential. Mathematically this implies that a whole set of analytical relations can be obtained by using any pair of the quantities P, V, T, S, E, etc., as independent variables. Only the more important relations used in calculating the functions from experimentally accessible data have been given above, but the general principle may be illustrated for the quantities E, S, V.

Taking any two independent variables x and y, since

$$dE = T\, dS - P\, dV,$$

$$\frac{\partial E}{\partial x} = T\frac{\partial S}{\partial x} - P\frac{\partial V}{\partial x}, \tag{1}$$

$$\frac{\partial E}{\partial y} = T\frac{\partial S}{\partial y} - P\frac{\partial V}{\partial y}. \tag{2}$$

Differentiating (1) with respect to y,

$$\frac{\partial}{\partial y}\frac{\partial E}{\partial x} = \frac{\partial T}{\partial y}\frac{\partial S}{\partial x} + T\frac{\partial}{\partial y}\frac{\partial S}{\partial x} - \frac{\partial P}{\partial y}\frac{\partial V}{\partial x} - P\frac{\partial}{\partial y}\frac{\partial V}{\partial x}, \tag{3}$$

and (2) with respect to x,

$$\frac{\partial}{\partial x}\frac{\partial E}{\partial y} = \frac{\partial T}{\partial x}\frac{\partial S}{\partial y} + T\frac{\partial}{\partial x}\frac{\partial S}{\partial y} - \frac{\partial P}{\partial x}\frac{\partial V}{\partial y} - P\frac{\partial}{\partial x}\frac{\partial V}{\partial y}. \tag{4}$$

The property of perfect differentials to be used is that the order of differentiation does not matter, i.e.

$$\frac{\partial}{\partial y}\frac{\partial E}{\partial x} = \frac{\partial}{\partial x}\frac{\partial E}{\partial y};$$

whence from (3) and (4)

$$\frac{\partial T}{\partial y}\frac{\partial S}{\partial x} - \frac{\partial P}{\partial y}\frac{\partial V}{\partial x} = \frac{\partial T}{\partial x}\frac{\partial S}{\partial y} - \frac{\partial P}{\partial x}\frac{\partial V}{\partial y}. \tag{5}$$

Any pair of S, V, T, P, etc., may now be chosen as the two independent variables x and y, for which, furthermore, since they are independent of one another, dx/dy may arbitrarily be put equal to zero.

Thus when $x = S$, $y = V$,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)$$

the change at constant entropy referring to adiabatic processes.

When $x = S$, $y = P$,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P.$$

When $x = T$, $y = P$,

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T.$$

When $x = T$, $y = V$,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

This particular set of equations is known as Maxwell's four thermodynamic equations, but by choosing other initial equations and going through the same procedure, a large number of relationships between the partial derivatives of these functions can be derived. Many of these are mathematical curiosities with no practical application.

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Thermodynamic functions and concentration of the components of a system

The dependence of the functions S, A, F, etc., on the concentrations of the various components which make up a system is important for many calculations. It is convenient to define Partial Molal Volume, Partial Molal Heat Content, etc., of the system by the equations

$$\frac{\partial V}{\partial n_1} = \overline{V}_1 \qquad \frac{\partial V}{\partial n_2} = \overline{V}_2$$

$$\frac{\partial H_1}{\partial n_1} = \overline{H}_1 \qquad \frac{\partial H_2}{\partial n_2} = \overline{H}_2 \quad ...,$$

where n_1, n_2, etc., are the number of moles of each component in the system. In general, since V is an extensive function,

$$dV = \left(\frac{\partial V}{\partial n_1}\right) dn_1 + \left(\frac{\partial V}{\partial n_2}\right) dn_2 ... = \overline{V}_1 dn_1 + \overline{V}_2 dn_2 ...,$$

with similar equations for the other functions, so that the result can always be written $V = \sum n_1 \overline{V}_1$, $H = \sum n_1 \overline{H}_1$, and all the equations derived for the thermodynamic functions of the system as a whole can be split up into formally similar equations for the partial molal quantities, e.g.

$$\overline{F}_1 = \overline{H}_1 - T\overline{S}_1.$$

When these partial molal equations are multiplied by the number of molecules of the component in question, and added, they give the corresponding equation for the system considered as a whole.

THERMODYNAMIC FUNCTIONS AND PHYSICO-CHEMICAL EQUILIBRIUM

In principle each of the functions S, A, F, ϕ can be used as a criterion of thermodynamic equilibrium, though the most suitable function to use depends on the physical restrictions on the system. The underlying idea is that in any system small local fluctuations in temperature, density, and energy are constantly arising, owing to the motions of the molecules, but that when the system is in equilibrium these fluctuations do not lead to a spontaneous change in the state of the system considered as a whole. The only direction in which a spontaneous change could occur is at once given from the second law of thermodynamics,

If the entropy is considered, this can only increase or remain unchanged, according to whether the change considered is irreversible or reversible. Formally this may be stated as follows: 'Keeping the volume and internal energy of the system constant, small fluctuations in the other variables must lead to a zero change in entropy if the system is in equilibrium, and to a positive change in entropy if the system is not in equilibrium', i.e.

$$\delta S \geqslant 0.$$

Similarly, at constant heat content small fluctuations must be subject to the condition $\delta F \leqslant 0$, or at constant internal energy to the condition $\delta A \leqslant 0$. If it is possible to express the dependence of the thermodynamic functions of a system on the concentrations of the components, etc., then the concentrations at equilibrium can be obtained by equating the first differential of the appropriate function to zero.

From a purely formal standpoint, the choice of which independent variables to use in expressing the thermodynamic properties of a system is summarized in a rule

given by Massieu. This states that the thermodynamic function whose maximum or minimum, at constant value of the independent variables, expresses the condition of equilibrium, gives the thermodynamic properties of the system by simple differentiation, i.e. in the most elegant form. The rule is best illustrated by a table. In the third set the results are described for the function ϕ, since those for the function F are closely related and have already been described.

Independent variables.   Equilibrium conditions.   Characteristic function.

(These have to be kept constant in calculating the effect of fluctuations in the dependent variables.)

E and V $\delta S = 0$ S

(i.e. no heat exchange with the surroundings)

giving (cf. p. 17) $\left(\dfrac{\partial S}{\partial E}\right)_V = \dfrac{1}{T}$ $\left(\dfrac{\partial S}{\partial V}\right)_E = \dfrac{P}{T}$

V and T $\delta A \leqslant 0$

giving $\left(\dfrac{\partial A}{\partial V}\right)_T = -P$ $\left(\dfrac{\partial A}{\partial T}\right)_V = -S$ (cf. p. 15)

P and T $\delta\phi \leqslant 0$

$$-S + \frac{(E + PV)}{T}$$

$$\left(\frac{\partial \phi}{\partial P}\right)_T = \frac{V}{T} \quad \left(\frac{\partial \phi}{\partial T}\right)_P = -\frac{H}{T^2}.$$

In connexion with this function it may be noted that

$$E = -T\left(T\frac{\partial \phi}{\partial T} + P\frac{\partial \phi}{\partial P}\right),$$

$$-S = \phi + T\frac{\partial \phi}{\partial T},$$

so that the thermodynamic behaviour is completely determined when ϕ is known as a function of T and P.

For practical purposes the most important function is the molal free energy, or for systems involving more than one component, the partial molal free energy. Before discussing how this is used for calculating equilibrium constants the

proof may be given that in a system at equilibrium the free energy/unit mass in each phase must be the same.

The condition for the coexistence of two phases of a substance in equilibrium is $\delta S = 0$, when the subordinate conditions are $\delta m = 0,\quad \delta E = 0,\quad \delta V = 0.$

Suppose the fraction x to be in phase 1, so that if m is the total mass of the system, the mass in phase 1 is mx and in phase 2 $m(1-x)$. If S_1 and S_2 are the entropies per unit mass in the two phases, the total entropy of the system is S, where

$$S/m = xS_1 + (1-x)S_2.$$

The total volume is V, where

$$V/m = xV_1 + (1-x)V_2.$$

The total energy is E, where

$$E/m = xE_1 + (1-x)E_2.$$

Applying the condition $\delta S = 0$, since m is constant,

$$x\,\delta S_1 + (1-x)\,\delta S_2 + (S_1 - S_2)\,\delta x = 0.$$

Now $$\delta S_1 = \frac{\delta E_1 + P_1\,\delta V_1}{T_1},\qquad \delta S_2 = \frac{\delta E_2 + P_2\,\delta V_2}{T_2}.$$

Eliminating δV_2 and δE_2 by means of these equations,

$$x\,\delta E_1\left[\frac{1}{T_1} - \frac{1}{T_2}\right] + x\,\delta V_1\left[\frac{P_1}{T_1} - \frac{P_2}{T_2}\right] +$$
$$+ \delta x\left[S_1 - S_2 - \frac{(E_1 - E_2)}{T_2} + P_2\frac{(V_1 - V_2)}{T_2}\right] = 0.$$

Since the variations δE_1 and δV_1 are independent, this equation can only be generally true if the intensive functions are the same, viz. $T_1 = T_2$, $P_1 = P_2$, and furthermore if

$$-S_1 + \frac{E_1 + PV_1}{T} = -S_2 + \frac{E_2 + PV_2}{T},$$

i.e. $$F_1 = F_2.$$

In the case of systems involving more than one component a similar proof shows that the partial free energy/unit mass must be the same in every phase. This quantity has therefore

been termed the thermodynamic potential of the component in question. If the molecular weight is chosen the same in every phase, the partial molal free energy must also be the same in every phase.

Finally, it must be noted that the definition of thermodynamic equilibrium rests upon the criterion of the effect of *small* fluctuations on the thermodynamic functions. This leads to a physically satisfactory treatment of equilibria such as the vapour pressure of solid nitric oxide, or the equilibrium

$$2H_2 + O_2 \rightleftharpoons 2H_2O,$$
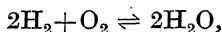
though if sufficiently large energy changes could take place within reasonable time the nitric oxide would change completely into nitrogen and oxygen at low temperatures, and the hydrogen and oxygen nuclei would probably change into helium atoms. Practically all thermodynamic equilibria are pseudo-equilibria in the sense that it is not the absolute minimum of free energy with respect to all possible changes which is discussed, but only with respect to changes which could take place within reasonable time.

Standard free-energy calculations and the equilibrium constant

For practical purposes the most useful criterion of equilibrium is $\delta F = 0$, since most experiments refer to processes taking place at constant pressure. Its application may be illustrated by calculating the free-energy change in a reaction between gases, such as $CO + H_2O \rightleftharpoons CO_2 + H_2$. Neglecting the correction for departures from the gas laws, which is irrelevant for the present purpose, the free-energy change on changing the concentration of any one component is

$$F_1 - F_2 = RT \ln C_1/C_2 \quad \text{(cf. p. 16)}.$$

This expression may be formally simplified by choosing for the standard state of reference the free energy F_2 at unit concentration (or one atmosphere pressure where partial pressures

are used), i.e. $C_2 = 1$. Writing the free energy in this standard state as F_0, the free energy in any other state is given by
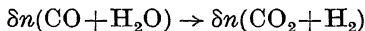
$$F_1 - F_0 = RT \ln C_1,$$

and the total free-energy change in the reaction is

$$\Delta F = \sum F_1 - \sum F_0 = RT \sum \ln C_1.$$

So far the C_1's have been left arbitrary; by selecting them to be any set of equilibrium concentrations for the mixture,

$$\sum F_1 = 0 \quad \text{and} \quad RT \sum \ln C_{eq} = -\sum F_0.$$

This follows from the fact that for an infinitesimal transformation of δn molecules in the equilibrium mixture

$$\delta n(CO + H_2O) \rightarrow \delta n(CO_2 + H_2)$$

the free-energy change

$$\delta n \sum F_1 = \delta F = 0$$

at equilibrium, so that

$$\sum F_{1\,eq} = 0.$$

Thus for any set of equilibrium concentrations

$$-\sum F_0 = RT \sum \ln C_{eq} = RT \ln K,$$

and since the left-hand side is a constant,

$$K = \text{constant},$$

where the equilibrium constant K is called the mass-action constant. The magnitude of the mass-action constant in terms of the standard free energies of the individual components is thus at once obtained in this method.

This equation is of fundamental importance in the application of thermodynamic functions to the calculation of equilibrium constants. It would, however, lead to no great practical progress if the only way of determining the thermodynamic functions experimentally were from studies on equilibrium constants, the electromotive force of reversible cells, and the limited number of other physicochemical measurements from which free energies can be calculated.

A much more general means of calculating thermodynamic

functions is from heat data, which can be obtained fairly easily in a large number of cases by direct calorimetry. The Gibbs-Helmholtz equation

$$\left(\frac{\partial F}{\partial T}\right)_P = -S = \frac{F-H}{T}$$

gives on transforming and integrating

$$\frac{F}{T} = \phi = - \int \frac{H}{T^2}\, dT \quad +I,$$

where I is an integration constant. (The same result is obtained even more directly by integrating the equation for ϕ on p. 20.) Thus values of F can be calculated from values of H provided the integration constant I is known. Since

$$F = -RT \ln K,$$

an alternative way of writing the above equation directly in terms of the equilibrium constant is

$$\ln K = \int \frac{H}{RT^2}\, dT \quad -I.$$

Using this formula, interpolation formulae for the values of F or K at different temperatures can be constructed from the following experimental data:

1. A knowledge of the value of H over the range of temperatures for which the interpolation formula is to be constructed. Since in any reaction $(\partial H/\partial T)_P = \sum C_P$ (cf. p. 9), it is always possible to write

$$H_{T_2} = H_{T_1} + \int\limits_{T_1}^{T_2} \left(\sum C_P\right) dT,$$

so that it is sufficient to determine experimentally the value of H at any one temperature, and the specific heats over the range of temperatures for which the formula is required.

2. In order to determine the integration constant I, the value of F at any one temperature is also required, and must be measured experimentally.

An alternative way of stating the problem of calculating

chemical equilibria from heat data may also be given, since it is useful in what follows. In any chemical equilibrium

$$n_1 A + n_2 B + ... \rightleftharpoons n_1' A_1' + n_2' B_2' + ...,$$
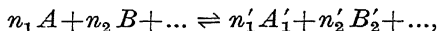
$$F = -RT \ln K = \sum n_r F_r,$$

where the suffix denoting that the free energies refer to the standard value at unit concentration is omitted, since no confusion arises.

This may be transformed into

$$F = \sum n_r (H_r - TS_r)$$
$$= \sum n_r H_r - T \sum n_r S_r$$
$$= H - T \sum n_r S_r,$$

where H is the change in heat content of the system. Thus the evaluation of F again resolves into an evaluation of H and of the individual entropies S_r of the substances taking part in the reaction. Since any entropy may be written

$$S_{T_1} = S_{T_2} + \int_{T_2}^{T_1} C_P \, d \ln T,$$

the construction of an interpolation formula for F as a function of temperature is again seen to require

(1) The determination of H at any one temperature.
(2) A knowledge of the values of C_P over the whole range of temperatures required.
(3) A determination of the individual entropies at any one temperature.

In a very large number of cases the experimental difficulties in evaluating the thermodynamic functions arise in determining at least one value of the free energy or entropy change in the reaction, since some sort of a reversible process has to be constructed and studied. It was with a view to eliminating the necessity for this measurement that the third law of thermodynamics was developed.

The evaluation of thermodynamic functions from heat data

The practical calculation of the functions H, S, F, etc., from calorimetric measurements alone rests upon two hypotheses first enunciated by Nernst,[†] and sufficiently verified and clarified since to be incorporated as the Third Law of Thermodynamics.

The evaluation of H: Nernst's first hypothesis.

The calorimetric determination of the change in heat content for a chemical reaction does not offer major experimental difficulties, provided a suitable temperature can be chosen for the measurement. The value of H at any other temperature can then be calculated from the equation

$$H_{T_1} - H_{T_2} = \int_{T_2}^{T_1} \left(\sum C_P \right) dT.$$

The value of H at absolute zero is of particular interest. In order to obtain it, it is necessary to extrapolate specific heat measurements below the lowest temperature of measurement. Nernst assumed that for 'condensed' phases (solids and liquids)

$$\lim_{T \to 0} \left(\frac{\partial H}{\partial T} \right)_P = \lim_{T \to 0} C_P = 0,$$

which means that the extrapolation from such low temperatures as can be readily obtained, to absolute zero, gives quite reliable values of the integral

$$\int_0^T C_P \, dT.$$

This is readily seen from Fig. 2. The theoretical expression $C_V = \alpha T^3$ obtained by Debye (cf. p. 66) is often used for the low-temperature extrapolation. Keesom has shown that for some metals $C_V = \alpha' T$ is closer to the experimental

results,† but the exact expression used makes little difference to the area under the curve, since $(\partial H/\partial T)_P$ is very small in either case.
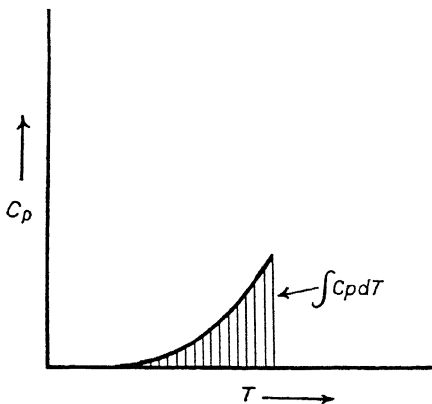

Fig. 2.

Evaluation of S; use of Planck's formulation of the heat theorem.

The evaluation of absolute entropies (i.e. entropies referred to the crystalline solid at absolute zero as standard) is a much more delicate problem than the evaluation of heat contents, and is one of the principal aims of contemporary thermodynamics. From S and H the value of F and of the equilibrium constant is readily computed. By definition,

$$S_P = \int C_P \, d\ln T \quad + S_0,$$

where S_0 is the entropy at absolute zero.

Planck first suggested that the entropy of crystalline bodies at absolute zero was probably zero, i.e. $S_0 = 0$. A less sweeping statement is that every body has a finite entropy which is *positive* but which may become zero at absolute zero for perfect crystalline substances. This form of stating

the heat theorem has the great advantage that it is much easier to see its statistical significance. Its connexion with Nernst's two original hypotheses

$$\lim_{T=0} \frac{\partial H}{\partial T} = 0 \quad \text{and} \quad \lim_{T=0} \frac{\partial F}{\partial T} = 0$$

is readily seen, since

$$\frac{\partial F}{\partial T} = \frac{\partial H}{\partial T} - S - T\frac{\partial S}{\partial T} = \frac{\partial H}{\partial T} - S - \frac{C_P}{T},$$

which only tends to zero at absolute zero if

$$S_0 = 0 \quad \text{and} \quad \lim_{T \to 0} C_P = 0.$$

The equations are written in the form of a *limit* to indicate that the approach to zero is asymptotic, i.e. that C_P decreases with T with a power of T greater than unity.

When the heat theorem applies, the calculation of entropies from experimental data merely involves an evaluation of the integral

$$S = \int C_P \, d\ln T,$$

since $S_0 = 0$. The difficulty of specific-heat anomalies at very low temperatures, in upsetting experimental evaluations of entropy, has already been referred to. The most direct test of how far such anomalies are widespread is to see how far the heat theorem applies to practical cases. It is useful to note that whenever an anomaly occurs at so low a temperature as to escape measurement, the entropy evaluated from specific-heat measurements will be too low, and can only be made to agree with the entropy evaluated by other means by giving S_0 a finite positive value. A number of apparent departures from the heat theorem can be explained in this way.

APPLICATIONS AND VERIFICATIONS OF THE HEAT THEOREM

THE method of applying the heat theorem in practice is best grasped from the methods used to test its validity.

(a) Verifications for condensed systems.

Whenever the equilibrium constant in a system involving only solid or liquid phases can be measured directly, a means is available for checking the heat theorem. The number of cases is not very large. One example is the calculation of the transition or equilibrium temperature between two solid phases. The method is simply to determine experimentally one value of H and the heat capacities over the whole range of temperatures. The absolute entropies are then calculated assuming Planck's law, and from the heat content and entropy the free energy and equilibrium constant are readily found. The result should agree within the limits of experimental error with the value determined directly.

Thus grey tin is an allotropic modification of white tin, and is less dense. Below 18° C. white tin tends to change spontaneously into grey tin, and above 18° C. grey tin tends to change spontaneously into white tin, this being the transition temperature under ordinary pressures. From specific-heat measurements extended to very low temperatures, assuming $S_0 = 0$ for both forms,

$$S_{25°C.} = 11 \cdot 17 \text{ (white tin)}, \quad S_{25°C.} = 9 \cdot 23 \text{ (grey tin)}.$$
$$\text{Difference } +1 \cdot 94.$$

(The entropy of the less stable form is necessarily smaller, since a spontaneous change at constant volume can only take place with increase of entropy.)

This result has to be compared with the directly determined value of $\Delta S_{\text{grey} \to \text{white}}$. ΔH is measured calorimetrically,

e.g. by dissolving each allotrope in acid in a calorimeter. ΔF is measured from the e.m.f. of a cell $\mathfrak{E}$,

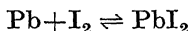<div align="center">grey tin | electrolyte | white tin,</div>

since the free-energy change for the passage of one faraday of electricity $\mathbf{F}$ is

$$-N\mathfrak{E}\mathbf{F} = \Delta F = -RT \ln K.$$

From the equation $\Delta F = \Delta H - T\Delta S$ the experimental value of $\Delta S = +1 \cdot 87$ (grey $\rightarrow$ white) is obtained. This compares very favourably with the value directly obtained from heat data.

Other systems involving only reactions between solids, which have been investigated, are

<div align="center">sulphur (rhombic) $\rightleftharpoons$ sulphur (monoclinic)</div>

$$\mathrm{Pb} + \mathrm{I}_2 \rightleftharpoons \mathrm{PbI}_2$$

$$\mathrm{Pb} + 2\mathrm{AgCl} \rightarrow \mathrm{PbCl}_2 + 2\mathrm{Ag}$$

$$\mathrm{Hg} + \mathrm{AgCl} \rightarrow \mathrm{HgCl} + \mathrm{Ag}.$$

The agreement in each case is within the limits of experimental error.

(b) *Verification from condensed systems in equilibrium with the gaseous phase.*

The heat theorem applies directly only to 'condensed' systems, and though at very low temperatures and high densities even gases probably show degeneracy, with $C_P \rightarrow 0$, no experimental measurements have been carried sufficiently far to make use of this fact in the evaluation of S. In consequence it is not possible to evaluate the absolute entropy of a gas using only thermal data and the laws of thermodynamics.

Statistical calculation (cf. p. 98) shows that the entropy constant $\mathfrak{A}$ of a monatomic perfect gas in the expression obtained on p. 14,

$$S = R\left[\ln \frac{T^{\frac{5}{2}}}{P} \mathfrak{A}\right],$$

is given by
$$\mathfrak{A} = \frac{(2\pi m k)^{\frac{3}{2}} k \, e^{\frac{5}{2}}}{\text{\small ?}},$$

where m is the mass of the molecule, k is Boltzmann's constant ($k = R/N$), and h is Planck's constant.

In terms of the atomic weight M this expression transforms to $S = R \ln(T^{\frac{5}{2}} M^{\frac{3}{2}})/P - 2 \cdot 300$ cals./° per mole, where the unit of pressure is the atmosphere. This statistical result may be used in a number of ways to verify the theorem that $S_0 = 0$ for crystalline substances.

I. The vapour-pressure equation for solids

The most direct way of verifying the heat theorem is from the vapour-pressure equation, either for solidified inert gases, or for metals such as Hg, Cd, Zn which give monatomic vapours.

On vaporization the entropy increase per mole is

$$\Delta S = S_{\text{gas}} - S_{\text{solid}} = \frac{\lambda}{T}$$
$$= \left[R \ln(T^{\frac{5}{2}} M^{\frac{3}{2}}) - R \ln P - 2 \cdot 30 \right] - \left[\int_0^T C_{P_s} \, d\ln T + S_0 \right],$$

where λ is the latent heat of vaporization per mole, C_{P_s} the specific heat of the solid, and S_0 the entropy of the solid at $0°$ K.

This expression is merely another way of writing the familiar vapour-pressure formula of a solid giving a monatomic vapour, since it transforms to

$$\ln P = \quad \cdot \frac{\lambda}{RT} + \tfrac{5}{2} \ln T - \frac{1}{R} \int C_{P_s} \, d\ln T + \left[\tfrac{3}{2} \ln M - \frac{2 \cdot 30}{R} - \frac{S_0}{R} \right],$$

or since
$$\lambda = \lambda_0 + \frac{5RT}{\text{\small 2}},$$

to

$$\ln P$$
$$= -\frac{\lambda_0}{RT} + \tfrac{5}{2} \ln T - \frac{1}{R} \int C_{P_s} \, d\ln T + \left[\tfrac{3}{2} \ln M - \left(\frac{S_0 + 2 \cdot 30}{R} \right) - \tfrac{5}{2} \right].$$

The temperature independent term in this equation is called the vapour-pressure constant i.

In testing the validity of the heat theorem it is usually more satisfactory to compare the entropy of the gas at any temperature, calculated directly from the equation

$$S_{\text{gas}} = R \ln T^{\frac{5}{2}} \mathfrak{A}/P,$$

with the experimental value determined from the vaporization process

$$S_{\text{gas}} = \lambda/T + S_{\text{solid}}.$$

In the experimental determination the entropy of the solid is taken as zero at the absolute zero, in accordance with the heat theorem, and the value of λ is computed from the slope of the vapour-pressure curve. Typical results at 25° C. and one atmosphere are

Gas	Experimental entropy	Calculated entropy
He	29·2	29·8
Ar	36·4	36·7
Cd	40·0	39·8
Hg	41·3	41·5

The good agreement provides a simultaneous check on statistical theory and on the heat theorem.

An older method, avoiding the explicit use of entropies, depends on the comparison of the vapour-pressure constant with the theoretical value. From the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\lambda}{(v_{\text{gas}} - v_{\text{solid}})T}.$$

At the very low pressures to which the experimental data refer $v_{\text{gas}} = RT/P$ per mole and $v_{\text{solid}} \ll v_{\text{gas}}$. The equation transforms to

$$\frac{1}{P}\frac{dP}{dT} = \frac{\lambda}{RT^2},$$

or

$$\ln P = \int \frac{\lambda\, dT}{RT^2} + i,$$

where i is the vapour-pressure constant. In this expression

$$\frac{d\lambda}{dT} = (C_{P(\text{gas})} - C_{P(\text{solid})}),$$

i.e.
$$\lambda = \lambda_0 + \int (C_g - C_s)\, dT,$$

so that
$$\ln P = -\frac{\lambda_0}{RT} + \int\int \frac{dT}{RT^2}(C_g - C_s)\, dT\ ;$$

or, using partial integration,

$$\ln P = -\frac{\lambda_0}{RT} + \frac{1}{R}\int (C_g - C_s)\, d\ln T - \frac{1}{RT}\int (C_g - C_s)\, dT + i.$$

This may be compared with the direct expression for the entropy of vaporization:

$$S_{\text{gas}} - S_{\text{solid}} = \frac{\lambda}{T} = \frac{\lambda_0}{T} + \frac{1}{T}\int (C_g - C_s)\, dT,$$

$$S_{\text{gas}} = \int C_g\, d\ln T - R\ln P + \mathfrak{A},$$

$$S_{\text{solid}} = \int C_s\, d\ln T + S_0.$$

Rewriting the equation for the entropy of vaporization,

$$\ln P = -\frac{\lambda_0}{RT} - \frac{1}{RT}\int (C_g - C_s)\, dT +$$
$$+ \frac{1}{R}\int (C_g - C_s)\, d\ln T - \frac{(S_0 - \mathfrak{A})}{R},$$

from which it follows that provided the same units of pressure are used, and provided the heat theorem applies for the solid phase ($S_0 = 0$),

$$i = +\frac{\mathfrak{A}}{R}.$$

(Some authors include the term $\dfrac{1}{RT}\displaystyle\int C_g\, dT$ in the value of i, since for a perfect monatomic gas it is independent of temperature and equal to $\tfrac{5}{2}$.) The theoretical value of the vapour-pressure constant is simply calculated from that of the entropy constant for the appropriate vapour, and is compared with the experimentally determined value.

II. Comparison of equilibrium constants with vapour-pressure constants

Although the use of free energy and entropy functions provides the most compact and general method of calculating equilibria, the vapour-pressure constants or 'theoretical chemical constants' have been frequently used in the past, particularly by German authors. The relation between the two different methods of calculation may be illustrated for the reaction $aA + bB + cC \rightleftharpoons dD + eE \ldots$.
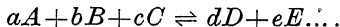
$$\Delta F = -RT \ln K = \Delta H - T \Delta S$$

$$= \Delta H_0 + \int_0^T (\sum C_P) \, dT - T \int_0^T (\sum C_{P_s}) \, d\ln T - T \sum S_{0(\text{solids})} -$$

$$- T \int_0^T (\sum C_{P(\text{gas})}) \, d\ln T - T \sum S_{0(\text{gases})}.$$

This expression may be rewritten

$$-\ln K = \frac{\Delta H_0}{RT} + \frac{1}{RT} \int \sum C_P \, dT -$$

$$- \frac{1}{R} \int \sum (C_{\text{solids}} + C_{g_i}) \, d\ln T - \sum \frac{S_{0(\text{solids})}}{R} - \sum \frac{S_{0(\text{gases})}}{R},$$

where S_0 refers to the entropy at $0°$ K., H_0 to the heat content at $0°$ K.

This may be compared with the reaction isochore,

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2},$$

which gives on integration

$$\ln K = \int \frac{\Delta H}{RT^2} + I.$$

Substituting for ΔH,

$$\ln K = -\frac{\Delta H_0}{RT} + \frac{1}{R} \int \frac{dT}{T^2} \int (\sum C_P) \, dT + I,$$

or integrating by parts,

$$\ln K = -\frac{\Delta H_0}{RT} - \frac{1}{RT} \int \sum C_P \, dT + \frac{1}{R} \int \sum C_P \frac{dT}{T} + I.$$

From a comparison with the previous expression it is seen that the integration constant

$$I = \sum \frac{S_{0(\text{solids})}}{R} + \sum \frac{S_{0(\text{gases})}}{R},$$

so that *if the heat theorem applies for solids, making*

$$\sum S_{0(\text{solids})} = 0,$$

the integration constant can be expressed in terms of the individual vapour-pressure constants, according to the equation

$$I = \sum \nu i = \sum \frac{S_{0(\text{gases})}}{R}$$

(ν is the number of molecules of the gas participating in the reaction).

It is thus possible to test whether the heat theorem applies to solids by comparing the calculated values of the integration constant with the sum of the individual vapour-pressure constants. Although heterogeneous equilibria are not so suitable for exact calculation as the vapour pressure of a single substance, on account of experimental errors, this method has the theoretical advantage that no appeal is made to statistical theory, since no use is made of the theoretical entropy constants of gases, provided the experimental vapour-pressure curves are known. This method is therefore directly applicable to equilibria involving polyatomic gases. Typical results may be listed as follows:†

Reaction	Limits of I (from reaction equilibrium)	Limits of $\sum \nu i$ (from vapour pressures)
$3H_2 + N_2 \rightleftharpoons 2NH_3$	-7.04 ± 0.10	-8.34 ± 0.09
$N_2 + O_2 \rightleftharpoons 2NO$	0.93 ± 0.28	0.61 ± 0.15
$2CO + O_2 \rightleftharpoons 2CO_2$	-0.8 ± 0.25	-1.38 ± 0.20
$H_2 + I_2 \rightleftharpoons 2HI$	-1.5 ± 0.12	-2.36 ± 0.22
$2CO \rightleftharpoons C + CO_2$	-0.86 ± 0.18	-1.01 ± 0.18
$2Hg_{(\text{vap})} + O_2 \rightleftharpoons 2HgO$	4.32 ± 0.18	4.44 ± 0.09
$CaO + CO_2 \rightleftharpoons CaCO_3$	0.9 ± 0.15	0.91 ± 0.15
$H_2 + HgO \rightleftharpoons Hg + H_2O$	-3.63 ± 0.16	-3.69 ± 0.03

† Eucken and Fried, *Zs. f. Phys.* **29**, 36 (1924).

In some cases the agreement is seen to be within the limits of uncertainty, which are rather large in this method of verification. Reactions involving hydrogen nearly always give very poor results. For reactions involving CO and NO the uncertainties of this method are too great, but a more precise method (cf. p. 74) shows that the discrepancy is real, and gives some clue as to its origin.

Theoretical chemical constants of polyatomic gases

Owing to their role in the integration of the reaction isochore, the vapour-pressure constants of the various components have been given the name of theoretical chemical constants. Once their value is known it is in principle possible to calculate all chemical equilibria from heat data alone.

The theoretical chemical constants of gases and the closely related entropy constants can be calculated from statistical theory. For monatomic gases the entropy constant $\mathfrak{A}$ in the expression $S_P = R \ln \dfrac{T^{\frac{5}{2}}}{P} \mathfrak{A}$ is $\mathfrak{A} = \dfrac{(2\pi mk)^{\frac{3}{2}} k e^{\frac{5}{2}}}{h^3}$. As is discussed later (p. 54) this entropy constant has to be multiplied by various factors if the atom or molecule of the gas is capable of taking up energy in other forms than translational energy, provided such activation is appreciable over the region of temperatures where the equilibrium is discussed. For the present purpose these rules may be summarized as follows:

(1) If the atoms have an electronic multiplicity $j > 0$, $\mathfrak{A}$ has to be multiplied by the factor $g = 2j+1$, since in the modified statistical calculation $2j+1$ atoms with closely similar but still distinguishable energy levels can now exist in the gas phase, for every atom which is there when the multiplicity is unity. This has been experimentally verified in the case of thallium, which has a ground state $^2P_{\frac{1}{2}}$ and $g = 2$, and a correspondingly larger entropy of vaporization.[†]

† Coleman and Egerton, *Phil. Trans.* **234**, 177 (1935).

(2) For polyatomic molecules the term $\mathfrak{A}$ has to be further multiplied by the factor for rotational energy

$$\frac{8\pi^2 I k}{h^2}\frac{1}{s}.$$

The moment of inertia $I = \sqrt[3]{(I_1 I_2 I_3)}$ of the molecule has to be evaluated from the separation of rotational bands in the band spectrum. The symmetry factor s only applies for symmetrical molecules such as N_2, O_2 for which it is 2 (cf. p. 120).

Practical calculation of the position of equilibrium in reactions

Before discussing the heat theorem further, the practical utilization of chemical constants may be referred to. For most purposes departures from the heat theorem do not much affect the value of the equilibrium constant calculated on the assumption that it holds. The only systematic method of calculating equilibria is to determine the entropy and heat-content functions for as many substances as possible, since from these the values of $\Delta F = -RT \ln K$ are at once obtained. The use of vapour-pressure constants is formally equivalent to this method, but in practice it leads to the tabulation of data from which the desired results can only be obtained with much more labour.

As an example of the calculation of equilibria not accessible by other means, the case of ionization in a star may be quoted.

In the process $\qquad A \rightleftharpoons A^+ + e$

the entropy change may be written

$$\Delta S = S_{A^+} + S_e - S_A \text{ per mole.}$$

Apart from changes in multiplicity of the atom on ionizing, which affect the entropy constants by affecting the factor g, but which will not be discussed here,

$$S_{A^+} = S_A \quad \text{and} \quad \Delta S = S_e.$$

For the equilibria in question the pressures are so low and

the temperatures so high that the electron gas is very dilute, and may be treated to a first approximation as a perfect monatomic gas of atomic weight $M = 0.000544$, from which the entropy constant of the electron gas can be calculated. Using the formula (p. 31),

$$\Delta S = S_e = \tfrac{5}{2}R\ln T + \tfrac{3}{2}R\ln M - 2.30$$
$$= 5\ln T - 24.70.$$

The change in heat content is approximately equal to the ionization energy per mole. If V is the ionization potential in volts,

$$\Delta H_0 = 23.3V \times 10^3 \text{ calories,}$$
$$\Delta H = \Delta H_0 + \int (C_A + C_e - C_{A^+})\, dT = \Delta H_0 + \frac{5RT}{2},$$

since $C_A = C_{A^+}$.

$$\therefore \Delta F = -RT\ln\frac{A^+e}{A} = 23.3V \times 10^3 - 5T\ln T + 29.7T$$

$$\log\frac{A^+e}{A} = -\frac{23.3V \times 10^3}{4.57T} + \frac{11.5}{4.57}\log T - \frac{29.7}{4.57}$$

$$= -\frac{5.1V \times 10^3}{T} + 2.5\log T - 6.5.$$

Since $V = 4$ to 5 volts for the alkali metals, the right-hand side is only positive when $T \geqslant 10^4\,°\mathrm{C}$. In the spectrum of the sun the lines for Na are strong, for K weak, and entirely absent for Rb and Cs. This is due to the fact that at the same temperature the abundance of unionized alkali metal, which is required for the spectrum, is largest for the metal with the largest ionization potential, as is clear from the above formula.

Approximation formula due to Nernst

For very rough calculations of the position of equilibrium in a reaction an approximation formula due to Nernst often gives quite reasonable estimates. This may be written

$$\log K_P = -\frac{\Delta H}{4.57T} + \sum n(1.75\log T) + \sum C,$$

where products are as usual accounted positive in the summations, and n refers to the number of molecules of each species taking part in the reaction. For reliable results $\sum n \not> \pm 1$. C is an empirical 'chemical constant' quite distinct from the vapour-pressure constant and only for use with this empirical formula. The following list has been given by Nernst.†

H_2	1·6	HCl	3·0	H_2S	3·0
N_2	2·6	HBr	3·2	SO_2	3·3
O_2	2·8	HI	3·4	CO_2	3·2
Cl_2	3·1	NO	3·5	NH_3	3·3
Br_2	3·2	CO	3·5	H_2O	3·6
I_2	3·9	N_2O	3·3		

For solids $C = 0$ and for atoms $C =$ half the value for the corresponding molecules. An example of how far equilibria can be represented by this formula is the reaction

$$H_2 + Cl_2 \rightleftharpoons 2HCl, \qquad \Delta H_{15°C.} = -44,000 \text{ cals.}$$

	$\log K_P$	
Temperature	obs.	calc.
300°	33·2	33·38
1,000°	10·43	10·93
2,000°	5·77	6·11

though the equation should be used with caution, since the values of C only fit a limited set of data.

† *The New Heat Theorem.*

TESTS AND FAILURES OF THE HEAT THEOREM

ACCORDING to the Nernst Heat Theorem as formulated by Planck, the absolute entropy of crystalline solids $S_0 = 0$ when $T = 0$. As formulated by Nernst,

$$\lim_{T \to 0} \frac{\partial H}{\partial T} = 0 = \lim_{T \to 0} \frac{\partial F}{\partial T}$$

for condensed systems.

The chief thermodynamic methods of verifying this theorem have already been referred to, and involve equilibria with one or more components. In principle, however, any method of studying the change of these functions with temperature, as the absolute zero is approached, will serve to test the theorem. An outstanding example is liquid helium.

Liquid helium

The properties of liquid helium are of considerable thermo-dynamic interest, since it is the only substance which remains liquid down to the lowest temperature attainable, and its thermal behaviour shows that the heat theorem is obeyed.

Surface tension. The change in free energy associated with surface changes is $\Delta F = \sigma \Delta \Omega$, where σ is the surface tension and Ω the area, so that the heat theorem would predict

$$\lim \frac{\partial \Delta F}{\partial T} = 0 = \lim \frac{d\sigma}{dT},$$

which is what is actually observed.

Change in melting-point with pressure. Although helium remains liquid down to the lowest available temperatures (0·8° K. or less) under its own vapour pressure, i.e. shows no triple point, it solidifies under pressure, the melting-point being 4·23° K. at 140·5 atm. and 2·15° K. under 25·3 atm.

As $T \to 0$ the melting-point curve tends to become parallel to the temperature axis. This is what would be expected from thermodynamical reasoning. The Clausius-Clapeyron equation states that the change of entropy on melting is ΔS, where
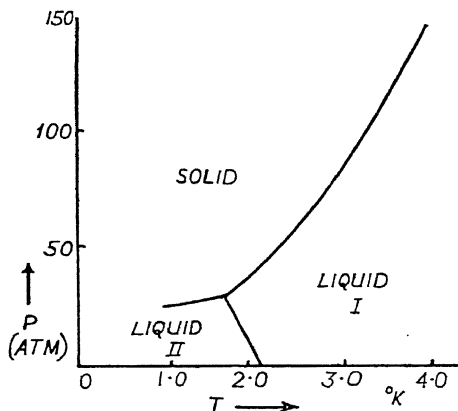
$$\frac{\Delta S}{\Delta \overline{V}} = \frac{dP}{dT},$$

FIG. 3.

and since $\Delta V \neq 0$ on melting, $\Delta S \to 0$ as $T \to 0$ means that $dP/dT \to 0$ if the heat theorem applies. This is what is actually found.

The fact that helium obeys the heat theorem, in spite of its remaining a liquid down to the lowest temperatures at ordinary pressures, implies that the liquid has some means of decreasing its entropy. This is probably connected with the transition into a second liquid form, Helium II, below $2 \cdot 3^\circ$ K. The transition can be followed from measurements on the density, surface tension, specific heat, etc. There is no latent heat change when liquid I is transformed into liquid II. This could only be expected on thermodynamic grounds if two immiscible liquids existed in equilibrium at the transi-

tion temperature. There is, however, a sharp maximum in the specific heat, similar to that observed in the ammonium-chloride effect (p. 75) and other internal transformations within a single phase. The slow rise on the low-temperature side and sharp fall on the high-temperature side are quite characteristic.

Evidence on the nature of Helium II is obtainable from thermodynamic considerations. Since the entropy change on melting progressively tends to zero as the temperature falls, and the solid has a progressively lower entropy on account of its state of order, and progressive decrease in heat content, the entropy of Helium II likewise gets progressively lower, suggesting it is in a state of quasi-crystalline order. A qualitative description is to compare Helium II with a crystalline solid in which the energy of the null-point oscillations $\frac{1}{2}h\nu$ of the atoms about their positions of equilibrium (cf. p. 61) exceeds the work required to shift an atom from one position to the next. The 'solid' thus shows no rigidity to shearing stresses, i.e. behaves apparently like a liquid. When the 'solid' is compressed sufficiently, the work of shifting the atoms from one position to the next in the lattice increases, and a finite rigidity is observed, marking the transition from Helium II to solid helium under increased pressure.

Supercooled liquids (glasses)

The case of helium, where the liquid form is in true equilibrium down to the lowest temperatures, is in sharp contrast with the class of supercooled liquids, or glasses, all of which fail to obey the heat theorem unless it is properly stated.

The ease with which a liquid can be cooled below the normal freezing-point is greatly increased as the number of associative groups such as hydroxyl is increased in the molecule. Typical glasses are given by glycerine and ethyl alcohol, and by the oxides and acidic salts of the oxides P_2O_5, As_2O_3, B_2O_3, SiO_2.

Two things favour the passage into a glass:

(*a*) The true crystal form is complex, so that the number of fresh crystallization nuclei formed in unit time below the melting-point is small.

(*b*) The rate of growth of the crystal on to a nucleus is small on account of the high viscosity. For substances
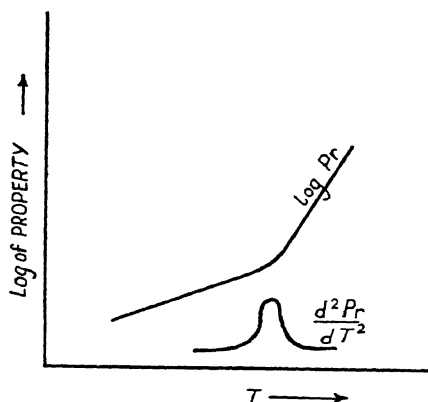

FIG. 4.

possessing these characteristics the properties of the super-cooled liquid can be studied with ease well below the melting-point. Thus the Heat Content, Volume, Viscosity, Dielectric Capacity, and Electrical Resistance for a supercooled liquid follow a general curve of the type shown in Fig. 4. To take one property of great importance for glasses, the viscosity of the liquid rapidly increases on cooling according to a law

$$\log \eta = -A + \frac{B}{T - T_\infty}$$

up to the temperature at which the glass becomes rigid. Over the small interval marked out on the curve $\frac{d^2 Pr}{dT^2}$, η increases from about 10^3 through the workable range of the glass (10^5 to 10^{10}) to the point of rigidity $\eta \simeq 10^{13}$. It may be

noted that a good glass that can be annealed without too much difficulty must not have the working range of temperatures too narrow. Tamman ascribes for example the change in the dielectric constant to the gradual rotation of permanent dipoles in the glass as the temperature is raised. The change from glass to supercooled liquid has thus certain analogies
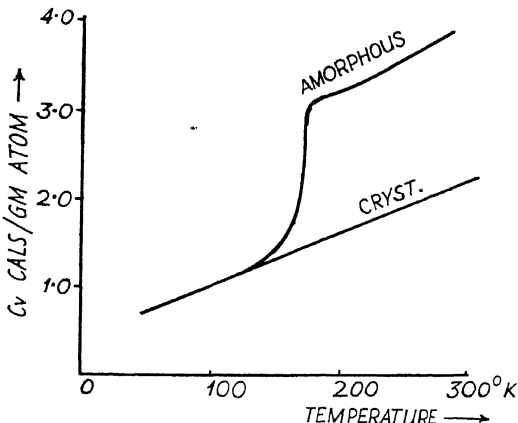

Fig. 5.

with the ammonium-chloride effect (p. 75), except that there is no change in crystalline form, associated with increasing rotation in the solid.

The entropy difference between a solid and the glassy supercooled liquid can be evaluated by careful specific-heat measurements from the melting-point down to very low temperatures. Fig. 5 shows the results obtained for glycerine by Lewis and Gibson. The initial drop for the solid compared with the liquid is due to the loss of heat contributions by atoms and groups when these are firmly bound. The gradual subsequent drop is due to the Debye oscillations of the lattice. The specific heat of the supercooled liquid remains approximately $3R/2$ above that of the solid, till the 'glass' is formed at about $180°$ K.; within a few degrees the

specific heat drops to the value for the crystal, since the very small differences in the characteristic frequency (cf. p. 64) of the crystal and glass are only noticeable at very low temperatures.

From these two curves the quantities S_{liquid} and S_{solid} can be calculated at the melting-point. If $S_0 = 0$ for both solid and glass, the equation

$$\Delta S_{\text{fusion}} = \frac{\lambda_{\text{fusion}}}{T} = S_{\text{liquid}} - S_{\text{solid}}$$

should hold. Actually a discrepancy is found in the sense that S_0 for the glass must be taken about 4·6 entropy units above the value for the crystal, in order to obtain agreement at the melting-point. As has been explained on p. 28, such a positive value of S_0 is sometimes due to a transition below the lowest temperature of measurement making a contribution to the entropy. In a glass such a transition is, however, very unlikely, and the conclusion is that glassy glycerine does not obey the heat theorem. For other glasses which have been measured discrepancies of the same order of magnitude have been found. This result is not very surprising, since from the point of view of thermodynamics the transitions crystal–glass or liquid–glass are not really reversible, and if a molecule escapes from the glass, the structure on recapture and energy gained are to some extent indeterminate, since it has not to occupy a definite position in the lattice, as it would in a crystalline solid.

The entropy of mixing: solid solutions and the heat theorem

The general expression for the entropy increase on allowing two perfect gases to mix by diffusion, keeping the total pressure constant, is readily obtained. For each component separately, before mixing,

$$S_1 = n_1(C_{P_1} \log T - R \log P_1 + k_1),$$
$$S_2 = n_2(C_{P_2} \log T - R \log P_2 + k_2),$$

where the initial pressures of the n_1, n_2 moles are $P_1 = P_2 = 1$ and the entropy constants are k_1, k_2. For the mixture,

$$S = \sum n_1 (C_{P_1} \log T - R \log P'_1 + k_1),$$

where P'_1, etc., are the partial pressures

$$P'_1 = n_1 P/(n_1 + n_2) = C_1 P,$$

i.e. $$S = \sum n_1 (C_{P_1} \log T - R \log C_1 P + k_1).$$

The entropy increase on irreversible mixing by diffusion is thus

$$\Delta S = S - (S_1 + S_2) = -R \sum n_1 \log C_1.$$

Dividing by $(n_1 + n_2)$, $\Delta S = -R \sum C_1 \log C_1$ per mole. Two interesting questions arise with respect to this result. The first is known as the Gibbs paradoxon. Gibbs pointed out that if the molecules of the two gases were not distinguishable by experiment, there should be no entropy increase on mixing, since the case could not then be said to differ from that where two identical portions of gas at the same pressure are put into communication. In such a case the molecules still interdiffuse, spontaneously, but there is no entropy increase when they do so. The question arises, how far must the molecules of the two gases differ for the result still to hold?

As will be seen later, the entropy increase on mixing has been confirmed even for mixtures of rotational isomers such as ortho- and para-hydrogen; for mixtures of isotopes experiments are not yet available but probably give the same result. The conclusion is that as long as molecules are distinguishable for statistical purposes the mixture law holds.

A second difficulty arises for solid solutions. Exactly the same expression for the entropy increase on mixing holds for dilute solutions as for gases, provided the solutions obey Raoult's law. According to the heat theorem, however, the entropy change in the process pure components → mixture,

$$\Delta S = S_{\text{mixture}} - \sum S_{\text{components}},$$

must decrease to zero towards absolute zero, since only con-

densed phases are involved. At first sight it would appear to be necessary to abandon the heat theorem for mixtures. Statistical considerations suggest, however, that the solution or mixture may have a number of ways of decreasing its entropy with falling temperature, and thus of approximating to the heat theorem, though in practice the processes involved may occur so slowly that experiments on solid solutions do not reveal them. One of these processes is the formation of ordered from disordered alloys (cf. p. 79), with a decrease in entropy of the solid solution. For gases it should further be noted that the mixture formula would have to be modified when degeneracy becomes appreciable, since the expression used for the entropy is then no longer valid.

Other departures from the heat theorem, such as solid hydrogen, carbon monoxide, and nitric oxide, are best discussed in terms of statistical theory, and are referred to later (p. 104 for hydrogen; p. 74 for CO and NO).

STATISTICAL THEORY AND THERMODYNAMIC FUNCTIONS

A RIGOROUS development of statistical mechanics requires a treatise of its own, and will not be attempted here.† Elementary statistical theory is, however, required in order to follow (1) the thermodynamical theory of the solid state, especially the heat theorem, and (2) the computation of thermodynamical functions for polyatomic gases from spectroscopically determined energy levels.

In applying statistical theory to the calculation of thermodynamic functions two main issues arise. In the first place, it is necessary to know all the energy states of any importance which can be 'occupied' by the molecules in the system under discussion. This is a physical problem, and does not require statistics. As will be seen in what follows, for solid systems it is necessary to devise suitable approximations to these energy levels in order to calculate the thermodynamic functions at all. For gases, on the other hand, the object is to use the experimentally determined energy levels from band spectra. The second and purely statistical problem is to determine the average number of the molecules of the system occupying any energy state. Once this average number is known it is fairly easy to calculate all the thermodynamic functions required.

Boltzmann's theorem for the most probable distribution of molecules

In statistical theory it is much easier to calculate the most probable distribution of molecules amongst the different energy levels than the average distribution. The difference arises from the fact that the molecules of the system need

† Cf. Fowler, *Statistical Mechanics*, 2nd ed. Cambridge, 1936.

not exist in the most probable distribution all the time, but might fluctuate and occupy less probable distributions part of the time, thus altering the average distribution. The theory of fluctuations shows, however, that such departures from the most probable distribution are insignificant provided the number of molecules over which the average is taken is sufficiently large, i.e. that it is quite safe to calculate thermodynamic functions from the most probable distribution, provided the calculation is restricted to macroscopic systems.

An elementary proof of Boltzmann's theorem for the most probable distribution of molecules among different energy levels may be developed as follows:

Consider a system with possible energy states

$$\epsilon_0, \epsilon_1, \epsilon_2, ..., \epsilon_r, ...$$

and with N molecules in all. Any one distribution may be characterized by saying that it refers to n_0 molecules in the state ϵ_0, n_r in the state ϵ_r, etc.

If there are no special restrictions (cf. p. 94), the number of ways of realizing this distribution is simply

$$W_{n,r} = \frac{N!}{n_1! \, n_2! \, n_3! \, ... \, n_r! \, ...}. \tag{1}$$

The most probable distribution is that for which this expression is a maximum, i.e. *the probability of a distribution is assumed proportional to the number of ways of realizing it.*

Any distribution is, however, subject to a number of physical conditions. In the present case these are

(1) That the total number of molecules is constant, i.e.

$$\sum n_r = N = \text{const.} \tag{2}$$

(2) That the total energy is constant, i.e.

$$\sum n_r \epsilon_r = E = \text{const.} \tag{3}$$

In order to determine the maximum probability W_e of W_{nr} it is necessary to have $\delta W_{nr} = 0$, or

$$\delta \ln W_{nr} = 0 = \delta \ln N! - \sum \delta \ln n_r!. \tag{4}$$

H

When the numbers n_r are large, the factorials may be evaluated, using Stirling's theorem, in the form

$$\ln n_r! = n_r \ln n_r - n_r. \tag{5}$$

When they are not large, statistical theory either does not apply in this simple form, or the states in question make a negligible contribution to the behaviour of the whole.

From equation (2) $\sum \delta n_r = 0$, $\tag{2'}$

and from (3) $\sum \epsilon_r \delta n_r = 0$. $\tag{3'}$

Applying (2') and (5) to (4), since N is constant, this gives

$$\delta \ln W_{nr} = 0 = - \sum \delta n_r \ln n_r. \tag{4'}$$

Multiplying (2') and (3') by arbitrary multipliers λ and μ and adding to (4'), these equations may be summarized in the form

$$\sum \delta n_r (\ln n_r + \lambda + \mu \epsilon_r) = 0, \tag{6}$$

which includes all the restrictions on the variations δn_r applying to the present problem. Since the values of δn_r in equation (6) are quite arbitrary apart from such restrictions, the only way the equation can be satisfied is for each of the equations $\ln n_r + \lambda + \mu \epsilon_r = 0$

to hold separately, i.e.

$$n_r = B e^{-\mu \epsilon_r}, \tag{7}$$

where $B = e^{-\lambda}.$

This equation gives the most probable distribution of molecules in a very simple case, but Boltzmann's theorem applies to a very large number of physico-chemical problems, unless these involve other restrictions than those considered. In order to use it in practice two points may be mentioned:

(a) Evaluation of the constants λ and μ in terms of physical magnitudes. For the example chosen this can most readily be done by comparing the expression obtained with the concrete case of a perfect gas. Thus the total energy E of the N molecules is

$$E = \sum n_r \epsilon_r = B \sum \epsilon_r e^{-\mu \epsilon_r},$$

and the average energy E/N per molecule is

$$\frac{B \sum \epsilon_r e^{-\mu\epsilon_r}}{B \sum e^{-\mu\epsilon_r}} = \bar{e},$$

i.e.
$$\bar{e} = \frac{E}{N} = \frac{\sum \epsilon_r e^{-\mu\epsilon_r}}{\sum e^{-\mu\epsilon_r}} = -\frac{\partial}{\partial\mu}\ln \sum e^{-\mu\epsilon_r}.$$

For a perfect monatomic gas the energy states ϵ_r refer to the translational energy, i.e.

$$\epsilon_r = \tfrac{1}{2}m(p_1^2 + p_2^2 + p_3^2),$$

where m is the mass of the molecule and p_1, p_2, p_3 are the momenta corresponding to the rth state, measured along any three axes at right angles. Since these can take up a continuous range of values, the summation may be replaced by an integration, i.e.

$$N = \sum n_r = B \sum e^{-\mu\epsilon_r}$$
$$= B \iiint\iiint e^{-(\mu/2m)(p_1^2+p_2^2+p_3^2)} dp_1 dp_2 dp_3 dx_1 dx_2 dx_3$$
$$= Bv \iiint e^{-\mu(p_1^2+p_2^2+p_3^2)/2m} dp_1 dp_2 dp_3,$$

where v is the volume containing the N molecules.

If E is the total energy of the gas, the value of p for any single molecule must lie within the limits

$$\sqrt{(2mE)} > p > -\sqrt{(2mE)}.$$

These limits when inserted in the integral give values practically the same as when the integration is carried out from $+\infty$ to $-\infty$, owing to the shape of the curve $y = e^{-(\mu/2m)p^2}$.

Inserting the limits ∞, $-\infty$, which give a definite value to the integral,

$$N = Bv\left(\frac{2m\pi}{\mu}\right)^{\frac{3}{2}}.$$

Similarly,
$$E = \frac{Bv}{2m}\frac{3}{2}\left(\frac{\pi^3(2m)^5}{\mu^5}\right)^{\frac{1}{2}};$$

whence
$$\mu = \frac{3N}{2E}, \qquad B = \frac{N}{v}\left(\frac{\mu}{2\pi m}\right)^{\frac{3}{2}}.$$

For a perfect gas,
$$PV = \tfrac{2}{3}E = N/\mu = RT$$

and $$\mu = \overline{\frac{}{kT}}.$$

Thus the most probable distribution of molecules among the different energy states is given by the expression

$$n_r = Be^{-\epsilon_r/kT},$$

where B is a constant determined by the physical properties of the system. The fact that

$$\mu = \frac{1}{kT}$$

depends on the role of μ in the various thermodynamic functions for any system of molecules, when these are expressed in terms of the Boltzmann distribution (cf. pp. 53 seq.), and is true for every physico-chemical system for which this distribution holds.

Quantum weights

In a number of physical problems a group of energy states $\epsilon_r, \epsilon_{r+1}, ..., \epsilon_{r+q}$ can arise in which the energy difference between ϵ_r and ϵ_{r+q} is very small compared with the interval to the next group of states. The group of q states is then conveniently taken together as a single state of quantum weight q, i.e. instead of writing

$$n_r = Be^{-\epsilon_r/kT},$$
$$n_{r+1} = Be^{-\epsilon_{r+1}/kT}, \text{ etc.}$$

the expression $\quad n_r = Bq_r\, e^{-\epsilon_r/kT}$

is used for the whole group, which for purposes of calculation is equivalent to a single state of quantum weight q_r.

The partition function (Planck's 'Zustandsumme')

In any physical problem the distribution of molecules in the different energy states can be conveniently summarized, in virtue of Boltzmann's theorem, by the partition function

$$Z = q_0\, e^{-\epsilon_0/kT} + q_1\, e^{-\epsilon_1/kT} + ... + q_r\, e^{-\epsilon_r/kT} ....$$

This expression merely sums the number of molecules in

each energy state, but as a result of its structure it can be directly connected with the thermodynamic functions already described.

Particular attention should be paid to the different evaluations of the energy levels used by different authors. One consistent method is to use the free atoms in the ground states as zero (cf. p. 57), in order to express the energy of the molecules. As defined here, the energy ϵ_0 of the ground state of the molecule is merely equal to the spectroscopically calculated zero-point energy. The only practical advantage this has over using the free atoms is that the dissociation energy is not always known as accurately as the energy differences $\epsilon_r - \epsilon_0$.

Relation between Z and the number of molecules N in the system.

According to Boltzmann's theorem the number of molecules in the rth energy state may be written

$$n_r = Bq_r\, e^{-\epsilon_r/kT},$$

where B is a constant of proportionality. The total number of molecules in the system is thus $N = B \sum q_r\, e^{-\epsilon_r/kT}$, i.e.

$$N = BZ.$$

Relation between Z and the internal energy E.

The average energy $\bar{e}$ per molecule is given by the expression

$$\bar{e} = \frac{E}{N} = \frac{B \sum \epsilon_r q_r\, e^{-\epsilon_r/kT}}{B \sum q_r\, e^{-\epsilon_r/kT}}.$$

The numerator is $-\dfrac{\partial Z}{\partial\{1/kT\}} = -\dfrac{\partial Z}{\partial\mu}$; the denominator is Z,

i.e.
$$\bar{e} = -\frac{1}{Z}\frac{\partial Z}{\partial\mu} = -\frac{\partial \ln Z}{\partial\mu},$$

$$E = N\bar{e} = -N\frac{\partial \ln Z}{\partial\mu}.$$

For a *perfect gas*, $H = E + RT$ per mole. It is clear that this is equivalent to writing

$$H = -N \frac{\partial \ln(Z/\mu)}{\partial \mu}$$

since

$$\frac{\partial \ln \mu}{\partial \mu} = \frac{1}{\mu} = \frac{RT}{N} .$$

Relation between Z and the specific heats.

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial E}{\partial \mu} \frac{\partial \mu}{\partial T} = \frac{\partial E}{\partial \mu} \left(- \frac{}{kT^2} \right. \qquad \left. - k\mu^2 \frac{\partial E}{\partial \mu} \right.$$

$$= R\mu^2 \frac{\partial^2 \ln Z}{\partial \mu^2} \text{ per mole.}$$

$$C_P = \frac{\partial H}{\partial T} = R\mu^2 \frac{\partial^2 \ln(Z/\mu)}{\partial \mu^2} \text{ per mole.}$$

Complete partition function for several modes of energy intake.

When the molecule can take up energy as translational, vibrational, rotational, and electronic energy, these different energy intakes can frequently be treated as independent to a first approximation. When this is so, the complete partition function

$$G = Z_{\text{trans}} \times Z_{\text{vib}} \times Z_{\text{rot}} \times Z_{\text{elect}} \times \dots$$

is defined as the product of the separate partition functions. The reason for this definition is at once clear when it is noticed that the separate partition functions always enter into the expressions for the thermodynamic functions in the form $\ln Z$; if the different energy intakes are independent, they must contribute in an additive way to functions such as E. This is secured by taking the product of the partition functions for G (cf. p. 116).

Relation between Z and the available energy A.

From the Gibbs-Helmholtz equations (cf. p. 15),

$$A - E = T \frac{dA}{dT},$$

i.e.
$$E = A - T\frac{dA}{dT};$$

or, dividing by T^2,
$$-\frac{E}{T^2} = -\frac{A}{T^2} + \frac{1}{T}\frac{dA}{dT} = \frac{d}{dT}\left(\frac{A}{T}\right),$$

so that
$$\frac{A}{T} = -\int \frac{E}{T^2}\,dT = \int E\,d\left(\frac{1}{T}\right) = k\int E\,d\mu;$$

and using the value for
$$E = -N\frac{\partial \ln Z}{\partial \mu},$$

we have
$$\frac{A}{T} = -Nk\ln Z,$$

or
$$A = -RT\ln Z.$$

Proceeding in exactly the same way for F, it is clear that for a perfect gas $\quad F = -RT\ln(Z/\mu).$

From the property mentioned on p. 21 it follows that in a system in equilibrium *Z must be the same for any component in every phase.*

Choice of zero in the evaluation of thermodynamic functions from Z.

A problem of some delicacy is the choice of zero for the thermodynamic functions, when these have been evaluated from Z and are to be used in conjunction with thermodynamic functions evaluated in other ways, e.g. from thermal data and the heat theorem. Until the functions evaluated in different ways have been adjusted so as to be measured from the same zero, it is convenient to refer to the thermodynamic functions evaluated from thermal data, and referring to the crystalline solid at absolute zero as standard, as H.T. functions (heat theorem), and to thermodynamic functions evaluated from the complete partition function as T.N.S. functions (theoretical functions including nuclear spin effects; cf. p. 104).

The difference between H.T. and T.N.S. functions will be clear from a consideration of the different ways of evaluating the internal energy and entropy of a gas, since the other functions can be made up from these two. The H.T. function E refers to all the energy which would be given up on cooling the gas down to absolute zero at constant volume. Inspection of Fig. 5a shows that the T.N.S. function includes in addition the zero-point energy of the molecules, which is not thermodynamically observable in the mere process of cooling, i.e.

HEAT CONTENT | ENTROPY

OBSERVED HEAT CONTENT – COOLING AS LOW AS POSSIBLE (EFFECTIVELY 0°K)

OBSERVED ENTROPY–COOLING AS LOW AS POSSIBLE

APPARENT H.T. ZERO

UNDETECTED SPECIFIC HEAT ANOMALIES

TRUE H.T. ZERO

ENTROPY DUE TO NUCLEAR SPIN & ISOTOPE MIXTURES

ZERO POINT ENERGY

STATISTICAL ZERO (T.N.S.)

FIG. 5a.

$$E_{\text{H.T.}} = E_{\text{T.N.S.}} - E^0,$$

where E^0 is the zero-point energy per mole.

Adjustment of zero for energy.

In evaluating equilibrium constants from the equation

$$-RT \ln K = A = E - TS$$

it is necessary to use the correct zero for both E and S. In thermodynamic processes involving only one molecular species the zero for E cancels. In a chemical reaction, the zero for each molecular species must be such that the algebraic sum for products and reactants gives the thermodynamically observable heat of reaction at 0° K. With the partition function as defined on p. 53, this heat of reaction is automatically included in the equations on p. 58, but if A is evaluated calorimetrically or from Giauque's partition function (p. 60) it has to be introduced in the equations on p. 58 by a zero-point factor $e^{-\Delta E^0/kT}$. (See note on p. 60.)

Adjustment of the zero for entropy in the complete partition functions.

A further complication, which must be adjusted before T.N.S. functions can be used in conjunction with H.T. functions, is that the complete partition function G includes factors which are never affected by thermodynamic processes such as change of temperature or concentration. One of these is the nuclear-spin multiplicity (p. 117), which is not changed in thermal or chemical processes affecting the atoms; in consequence, the factor cancels out in all thermodynamic calculations. Another is the isotope effect. According to definition, the entropy of a mixture of two isotopes in proportions $x : (1-x)$ would be

$$S = xS_1 + (1-x)S_2 - x \ln x - (1-x)\ln(1-x),$$

where $x \ln x + (1-x)\ln(1-x)$ is the mixture term, but since no ordinary process affects the ratio of the isotopes the mixture term usually cancels.

If T.N.S. functions were used exclusively, no harm would be done by leaving in these factors in G, since they cancel whenever the functions are used in a calculation. They are, however, not included in the H.T. functions since e.g. the nuclear-spin multiplicity would not contribute to the specific heat till very low temperatures indeed.

The safest procedure is to subtract all terms from the T.N.S. functions which refer to effects which could not be observed in ordinary thermodynamic processes (cf. also pp. 117, 120).

It may be noted that some authors use the free atoms as zero of energy for the energy levels of the molecule. When this is done, *all* these levels differ from those discussed above by $\mathfrak{E}_D$, where $\mathfrak{E}_D$ is the dissociation energy of the molecule in its ground state, into unexcited atoms. The effect is simply to multiply the partition function by the term

$$Z_{\text{atom zero}} = e^{-\mathfrak{E}_D/RT} Z_{\text{molecule zero}},$$

I

and the adjustment of zero of the T.N.S. functions to correspond with H.T. functions offers no difficulty. In this case the zero-point energy factor is automatically included in the partition factor for vibrational energies.

Expression for F in terms of G.

After adjusting the zero of the complete partition function G by subtracting factors which refer to processes not observable thermodynamically, the complete expression for ΔF in a reaction $aA + bB + \ldots \rightleftharpoons mM + nN + \ldots$ is obtained as follows:

For the individual substances,

$$F_{\text{standard}} = -RT \ln \left[Z_{\text{int}} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{kT}{a} \right]$$

$$= -RT \ln \left[G \left(\frac{kT}{a} \right) \right],$$

where $G = Z_{\text{int}} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}},$

includes a constant a, the partition function Z_{int} for internal energies which are thermodynamically observable, and the factor $\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}}$ for translational energy in three degrees of freedom. The constant $a = 1$ atm. in dynes/cm². $= 1 \cdot 0132 \cdot 10^6$ is inserted since F_{standard} must refer to the gas at one atmosphere pressure.

Also $\Delta F_{\text{standard}} = -RT \ln K_p$

so that $K_p = \dfrac{G_M^m \, G_N^n \ldots}{G_A^a \, G_B^b \ldots} \left(\dfrac{kT}{a} \right)^{(\Sigma n - \Sigma b)}.$

By omitting the term $\left(\dfrac{kT}{a} \right)^{(\Sigma n - \Sigma b)}$, since $K_p = K_c \left(\dfrac{kT}{a} \right)^{(\Sigma n - \Sigma b)}$, the expression

$$K_c = \frac{G_M^m \, G_N^n \ldots}{G_A^a \, G_B^b \ldots} \qquad \text{(concentration in moles/c.c.)}$$

is obtained. It may be noted that the unit of pressure in K_p is the atmosphere, but that K_p may be obtained in c.g.s. units by omitting the factor a.

Relation between the partition function and the entropy.

Using the thermodynamic relation

$$S = \frac{E-A}{T},$$

it is easily seen that the value of S in terms of Z is

$$S = R\ln Z - \frac{N}{T}\frac{\partial \ln Z}{\partial \mu} = R\ln Z - R\frac{\partial \ln Z}{\partial \ln \mu}.$$

A more elegant expression for S was first obtained by Boltzmann, viz.

$$S = k\ln W_e,$$

where S is the entropy of the system, and W_e refers to the probability of the most probable distribution of molecules, which has already been discussed (cf. p. 49). This result may be obtained as follows:

Using the expression on p. 49,

$$\ln W_e = N\ln N - N - \sum n_r \ln n_r - \sum n_r.$$

But $n_r = Be^{-\epsilon_r/kT}$, where the q_r states of energy $\simeq \epsilon_r$ are all counted as separate, since they occur separately in W_e. Also

$$N = \sum n_r = B\sum e^{-\epsilon_r/kT} = BZ.$$

Substituting,

$$\ln W_e = N\ln Z + N\ln B - B\sum e^{-\epsilon_r/kT}\ln B + \sum Be^{-\epsilon_r/kT}\frac{\epsilon_r}{kT},$$

i.e. $$= N\ln Z + \sum \frac{n_r\,\epsilon_r}{kT},$$

or $$k\ln W_e = R\ln Z + \frac{E}{T} = \frac{E-A}{T} = S_{\text{T.N.S.}}$$

This expression makes the statistical significance of the heat theorem clear. If $S \to 0$ when $T \to 0$ this means that $W_e \to 1$ when $T \to 0$, i.e. that *all the molecules of the crystal pass into a unique energy state at the absolute zero.*

At present it is not possible to determine experimentally whether the heat theorem applies only to $S_{\text{H.T.}}$ or also to $S_{\text{T.N.S.}}$, i.e. whether the minute energy differences leading to nuclear-spin multiplicity would be resolved at $0°\,\text{K}$.

In passing, it may be noted that the various formulae just given make certain peculiarities of the thermodynamic functions much clearer.

Thus the fundamental formula

$$S = k \ln W_e$$

corresponds with the fact that entropies are additive and probabilities multiplicative. When a system moves into a more probable state, its entropy is increased and its probability is multiplied by a factor.

In the same way the equation

$$A = E - TS = -RT \ln K$$

corresponds with the fact that equilibrium depends both on the energy and probability of a system. At $0°$ K. the state of equilibrium is that for which E is a minimum, since $S = 0$, but at higher temperatures states of bigger probability and hence bigger entropy can be favoured in spite of the fact that they also have a bigger energy.

A further variation in writing the partition function is used e.g. by Giauque ($J.A.C.S.$ **52**, 4808 (1930)), in which the zero-point energy is not included in the energy levels, so that

$$Z_g = q_0 + q_1 e^{-\epsilon_1/kT} + q_2 e^{-\epsilon_2/kT} + \dots .$$

If it is desired to use this function the change can be readily made by writing
$$Z_g \times e^{-\epsilon_0/kT} = Z$$
in *all* the formulae quoted.

STATISTICAL ACCOUNT OF THE SOLID STATE

OWING to their important role in the heat theorem, theoretical expressions for the thermodynamic functions of a solid have received considerable attention. Apart from special effects, which will be mentioned later, the energy content of a solid is due to the vibrations of the atoms and molecules in the crystal, and the problem is to find workable approximations for the energy states which the atoms can occupy. Once such approximations have been found the distribution of the atoms amongst them follows the principles already discussed.

A. *Thermodynamic functions of a single oscillator.*

The simplest type of vibrational energy is that of a set of Planck oscillators of constant frequency ν, and capable of taking up quanta of energy $h\nu$, $2h\nu$,..., $rh\nu$,..., and so on.

For such a case

$$Z = q_0 e^{-\epsilon_0/kT} + q_1 e^{-(\epsilon_0+h\nu)/kT} + ... + q_r e^{-(\epsilon_0+rh\nu)/kT} + ...$$

All the quantum weights are unity, and the resulting infinite geometrical progression may be summed to

$$Z = e^{-\epsilon_0/kT}/(1 - e^{-h\nu/kT}),$$

giving

$$\bar{e} = h\nu/(e^{h\nu/kT} - 1) + \tfrac{1}{2}h\nu.$$

The term $\tfrac{1}{2}h\nu$ refers to the zero-point energy of the oscillators. The available energy per oscillator:

$$\bar{a} = kT \ln(1 - e^{-h\nu/kT}) + \tfrac{1}{2}h\nu.$$

Applying these results to crystalline solids, if all the atoms in the solid vibrated independently with the same frequency ν, the energy content of N atoms would be simply

$$E = N\bar{e} = Nh\nu/(e^{h\nu/kT} - 1) + \tfrac{1}{2}Nh\nu.$$

This elementary theory was first proposed by Einstein, but although it gives a specific heat $C_V = \partial E/\partial T$ falling to zero

towards absolute zero, as required by the heat theorem, the rate of decrease of the Einstein function is more rapid than experimental results actually show. The failure of the theory is due to the fact that the vibrations of the atoms in a solid lattice are not independent but coupled, since the displacement of any atom from its position of equilibrium affects the restoring force on each of its neighbours. For some purposes the thermodynamic functions of an 'Einstein' solid may be used to discuss its behaviour, especially as the detailed calculation of the frequencies arising in a three-dimensional solid is very laborious.

B. *The 'line' solid with coupled vibrations.*

It is frequently useful to consider the simpler case of a one-dimensional solid. Taking a row of atoms of equal masses (the so-called line solid) and assuming that the restoring force on any atom when displaced from equilibrium is solely due to the displacement relative to its two immediate neighbours, for a simple harmonic vibration of frequency ν the restoring force on the rth atom, if the displacement is X_r, will be

$$4\pi^2 m\nu^2 X_r = k(X_{r-1}-X_r)+k(X_{r+1}-X_r)$$

according to the above assumptions, since $X_{r-1}-X_r$ and $X_{r+1}-X_r$ are the displacements relative to the two immediate neighbours.

Writing as solution $X_r = a\cos rC$ and substituting

$$4\pi^2 m\nu^2 a\cos rC$$
$$= ak[\cos(r-1)C-\cos rC+\cos(r+1)C - \cos rC]$$
$$= 2ak\cos rC[\cos C-1],$$

i.e.
$$\cos C-1 = 2\sin^2 \tfrac{1}{2}C = \frac{2\pi^2\nu^2 m}{k},$$
$$\sin \tfrac{1}{2}C = \pi\nu\sqrt{\left(\frac{m}{k}\right)},$$

which gives a relation between the natural frequencies ν of

the line solid and the values of C. These are subject to the further condition that, since the ends of the solid must be free from constraint,

$$X_{n+1} = \cos(n+1)C = 0,$$

i.e. $(n+1)C = \tfrac{1}{2}(2j+1)\pi$, $C = \dfrac{2j+1}{2(n+1)}\pi$ $(n \geqslant j \geqslant 0)$,

and an analogous solution,

$$X_r = a \sin rC,$$

gives

$$X_{n+1} = \sin(n+1)C = 0, \quad C = \frac{2\pi j}{(n+1)} \quad (n \geqslant j > 0),\dagger$$

where j is an integer.

If b is the spacing of the atoms, the wave-length (i.e. the distances at which the disturbance is again in the same phase) is given by

$$\lambda = \left(\frac{2\pi}{C}\right) b,$$

from which the velocity of the disturbance, $v = \nu\lambda$,

$$v = \frac{2\pi b}{C} \frac{1}{\pi} \sqrt{\left(\frac{k}{m}\right)} \sin \tfrac{1}{2}C. \tag{1}$$

The line solid shows the characteristic phenomenon of dispersion, i.e. alteration of velocity with wave-length. For small values of C, λ is very large and $(\sin C)/C \simeq 1$,

$$v_\infty = b \sqrt{\left(\frac{k}{m}\right)} \qquad \text{from (1).}$$

The smallest value of λ is $2b$, $C = \pi$, for which

$$v_0 = \frac{2b}{\pi} \sqrt{\left(\frac{k}{m}\right)}, \qquad \frac{v_\infty}{v_0} = \tfrac{1}{2}\pi,$$

showing that the long waves have the larger velocity.

Three-dimensional lattice.

Although a similar dispersion must hold for the three-dimensional solid, the calculation of the individual frequencies for use in the partition function is not usually practicable.

† $C = 0$ is excluded since it makes the equations on p. 62 indeterminate.

A very successful first approximation to the problem has been developed by Debye, who treats the solid as an elastic continuum, i.e. neglects dispersion effects. For such a continuum the number of stationary oscillations or natural frequencies between λ and $\lambda + d\lambda$ is

$$dZ_\lambda = \frac{V}{\lambda^4} 4\pi \, d\lambda,$$

where V is the volume of the continuum.

Now if dispersion is neglected, i.e. taking a single velocity v for the vibrations,

$$\nu = \frac{v}{\lambda}, \qquad d\nu = -v\frac{d\lambda}{\lambda^2},$$

$$dZ_\nu = 4\pi V \nu^2 \, d\nu \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right), \tag{a}$$

where v_t are the two translational velocities of sound (taken as equal in an isotropic medium) and v_l is the velocity of any longitudinal vibration. Taking a mean velocity v_m such that

$$\frac{3}{v_m^3} = \frac{2}{v_t^3} + \frac{1}{v_l^3},$$

$$dZ_\nu = \frac{12\pi V \nu^2 \, d\nu}{v_m^3}.$$

In order to satisfy the further physical condition that the total number of degrees of freedom of a solid composed of N atoms is $3N$, an upper limit $\nu_{\max}$ is imposed on the possible frequencies such that

$$3N = \frac{12\pi V}{v^3} \int_0^{\nu_{\max}} \nu^2 \, d\nu,$$

or

$$3N = \frac{4\pi V}{v^3} \nu_m^3.$$

This equation makes it possible to eliminate the velocity and to write

$$dZ_\nu = \frac{9N\nu^2 \, d\nu}{\nu_m^3}.$$

Using this approximation for the possible energy states of

the atoms in the lattice, and the average energy e_ν of an oscillator of frequency ν, at temperature T (cf. p. 61), viz.

$$e_\nu = \frac{h\nu}{e^{h\nu/kT} - 1} + \tfrac{1}{2}h\nu,$$

the total energy content of the solid due to the vibrations of the lattice is

$$[E_\nu]_T = \int_0^{\nu_m} e_\nu \, dZ_\nu$$

$$= \frac{9N}{\nu_m^3} \int_0^{\nu_m} \nu^2 \, d\nu \left(\frac{h\nu}{e^{h\nu/kT} - 1} \right) + \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu^3 \, d\nu}{2}.$$

For purposes of calculation this expression is transformed by substituting
$$\frac{h\nu_m}{k} = \Theta, \qquad \frac{h\nu}{kT} = x$$

to a generalized function of (Θ/T), i.e.

$$[E_\nu]_T = 9RT \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \frac{x^3 \, dx}{e^x - 1} + \tfrac{9}{8}R\Theta.$$

In this expression the constant Θ is a characteristic temperature of the substance whose value depends on the elastic properties. This follows both from the direct derivation, from which

$$\Theta = \frac{\nu h}{k} \sqrt[3]{\left(\frac{3N}{4\pi V} \right)},$$

or from the theory of dimensions, according to which

$$\Theta = A \frac{h}{k} \frac{N^{\frac{1}{3}}}{m^{\frac{1}{3}} X^{\frac{1}{2}} \rho^{\frac{1}{3}}},$$

where M is the atomic weight, X the compressibility, ρ the density, and the constant of proportionality A is approximately the same for substances of the same lattice structure. These expressions are occasionally useful in estimating the thermodynamic functions of a solid from calculated values of Θ in the absence of experimental data on the specific heat, but should be used with caution. Tables of the values of this

integral for various values of (Θ/T) are given by Landolt and Bornstein.† The values of $C_V = \partial E/\partial T$ are obtained by direct differentiation of the expression for E, which gives (writing $y = \Theta/T$)

$$C_V = 9R\left[\frac{4}{y^3}\int\limits_0^y \frac{x^3\,dx}{e^x-1} - \frac{y^4}{e^y-1}\right].$$

At temperatures such that Θ/T is small, the value of C_V tends to $3R$ per gramme atom, the Dulong and Petit value for the atomic heat of solids. At low temperatures, where Θ/T is large and oscillations of high frequency make negligible contribution to the specific heat, the integral

$$\int\limits_0^{\Theta/T} \frac{x^3\,dx}{e^x-1} \quad \text{approximates to} \quad \int\limits_0^\infty \frac{x^3\,dx}{e^x-1} = \frac{\pi^4}{15}.$$

Thus

$$E_\nu = 9RT\left(\frac{T}{\Theta}\right)^3 \frac{\pi^4}{15}$$

and

$$C_V = \frac{12}{5}R\frac{T^3}{\Theta^3}\pi^4 = aT^3,$$

where a is a constant depending only on the characteristic temperature of the solid.

It will be noted that this expression for the specific heat satisfies the postulate of the heat theorem that

$$\lim_{T\to 0}\frac{\partial H}{\partial T} = 0.$$

For solids with simple cubic lattices the theory has been verified over a range of temperatures by calculating the Θ value at each temperature from the observed value of C_V, making use of the tables already referred to. If the theory were to apply rigorously, Θ should be independent of temperature. Actually a drift in the values of Θ is nearly always found,‡ though in many cases the change in Θ does not exceed 5 per cent. over practically the whole range where Θ varies with temperature.

† *Tabellen*, 5th ed.   ‡ Cf. Blackman, *Proc. Roy. Soc.* **148** A, 365 (1935).

At low temperatures the result $C_V = aT^3$ is found to apply even to complicated non-isotropic solids such as

$$CaF_2, \quad (NH_4)Cl, \quad SiC,$$
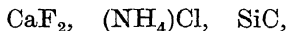
and both crystalline and glassy quartz and glycerine. This is probably connected with the fact that at low temperatures the wave-lengths of vibrations which still contribute to C_V are large compared with the lattice spacing, so that the treatment of the solid as a continuum involves fewer inaccuracies.

Thermodynamic functions and equations of state for the Debye solid

In view of the approximate nature of Debye's theory, graphical integration of the experimentally determined specific heat should be used in calculating the thermodynamic functions whenever suitable data are available. The equation of state of the Debye solid is, however, occasionally useful, and may be developed as follows:

Assuming the heat theorem to apply to the solid, and choosing the solid at absolute zero as standard state, the available energy A at any temperature is given by

$$A = -T \int^{T} \frac{E}{T^2} \, dT,$$

where the value of E has to be inserted from Debye's expression

$$E = 9RT \int^{\Theta/T} \frac{x^3 \, dx}{e^x - 1}$$

(omitting zero-point energy, cf. p. 56). This gives

$$A = -E/3 + 3RT \int^{y} \frac{dy}{e^y - 1}$$

$$= 3RT \left\{ -\left(\frac{T}{\Theta}\right)^3 \int^{y} \frac{y^3 \, dy}{e^y - 1} + \int^{y} \frac{dy}{e^y - 1} \right.$$

where $y = \Theta/T$ as before. This is the available energy of the solid at temperature T but still at the constant volume V_0 it occupied at absolute zero. In order to calculate the available energy at temperature T and at zero external pressure, volume V, the solid may be compressed at $0°$ K. to the volume V, and then heated to T at this constant volume. If W is the work of compression,

$$A = W + 3RT\left\{-\left(\frac{T}{\Theta}\right)^3 \int_0^y \frac{y^3\,dy}{e^y-1} + \int_\infty^y \frac{dy}{e^y-1}\right\},$$

where the value of Θ (which varies with the volume) now corresponds to the volume V.

To obtain the equation of state the equation

$$p = -\left(\frac{\partial A}{\partial V}\right)_T$$

is used. This gives

$$p = -\frac{dW}{dV} - 9RT\frac{1}{T}\frac{d\Theta}{dV}\left(\frac{T}{\Theta}\right)^4 \int_0^{T/\Theta} \frac{y^3\,dy}{e^y-1},$$

or multiplying through by V and noting that $\dfrac{d\Theta}{dV} = \dfrac{\Theta}{V}\dfrac{d\ln\Theta}{d\ln V}$, on transposing,

$$pV + V\frac{dW}{dV} = -\frac{d\ln\Theta}{d\ln V}9RT\left(\frac{T}{\Theta}\right)^3 \int_0^y \frac{y^3\,dy}{e^y-1}$$

$$= -\frac{d\ln\Theta}{d\ln V}E_\nu = YE_{\gamma'},$$

where E_ν is the thermal energy due to the oscillations of the lattice. From this equation of state such properties as the coefficient of expansion $\dfrac{dV}{dT}$ are readily obtained.

It may further be noted that the change in Θ with V is due to the fact that when the solid expands the increased separation of the atoms leads to changes in the mutual forces they exert on one another, and consequently to changes in

$\nu_m = \dfrac{k\Theta}{h}$. Furthermore, the Debye solid at low temperatures obeys the heat theorem, since $A = -\beta T^4$,

$$C_V = 12\beta T^3 = -T\frac{\partial^2 A}{\partial T^2}.$$

Other aspects of the vibrational heat content of solids

Attempts have been made to improve on the theory of the solid treated as a continuum by allowing for the increase in velocity of the waves with increasing wave-length. Inspection of equation (a) on p. 64 shows that in the $3N$ vibrations available there must be relatively more of high frequency, where the velocity is smaller, than is allowed for in the theory of Debye. This probably explains the success of the empirical equation proposed by Nernst and Lindemann,†

$$[E_\nu] = \tfrac{1}{2}E(\nu) + \tfrac{1}{2}E(\nu/2),$$

where $E(\nu)$ is the energy/gm. mole for oscillators all with frequency ν, i.e. (cf. Blackman, l.c.)

$$E(\nu) = \frac{Nh\nu}{e^{h\nu/kT} - 1} \cdot \frac{Nh\nu}{2} \quad \text{(cf. p. 61).}$$

For solids made up of complicated molecules, such as ice, the vibrations of the lattice as a whole are often practically independent of the internal vibrations of the molecule. In such a case the Debye theory may be applied to the vibrations of the lattice and the Einstein expression to the internal oscillations of the molecules: $[E_\nu]$ is simply the sum of Debye and Einstein functions,

$$[E_\nu] = D(\Theta_1) + E(\Theta_2) + E(\Theta_3), \text{ etc.}$$

At temperatures approaching the melting-point of the solid the displacements of the atoms from their mean positions no longer obey Hooke's law, i.e. the restoring force is no longer proportional to the displacement. The

† *Zeit. f. Electrochemie,* **17,** 817 (1911).

resulting anharmonic lattice vibrations increase the specific heat by a linear term

$$C_V = 3R + \alpha T,$$

though in practice it is seldom possible to disentangle this effect from other factors leading to an increase in the specific heat above the Dulong and Petit value.

Other sources of the heat content of solids

Besides being able to take up vibrational energy, the atoms and molecules in a crystal lattice can increase their energy content in a number of other ways. Such changes in energy of the atoms are of considerable importance for the theory of lattice structure and have a direct bearing on apparent departures from the third law of thermodynamics.

For purposes of calculation, the simplest of such effects is that first discussed by Schottky. It refers to a solid in which the atoms or molecules can occupy two different energy states, numbered 1 and 2, with energy difference ϵ. The value of ϵ for any atom is assumed *independent* of the states of the neighbouring atoms, i.e. of the number already in the higher state. Even though such cases are seldom realized in practice, the calculation illustrates a number of features shown by nearly all energy transitions even when these are much more complicated.

When the transition energy ϵ is independent of the number N_2 of atoms in the higher state, the ratio relative to the number N_1 in the lower state is given by the Boltzmann expression

$$\frac{N_2}{N_1} = q e^{-\epsilon/kT},$$

where q is here the *ratio* of the quantum weights of the two states. The average energy per molecule due to this effect will be

$$\bar{e} = \frac{N_2 \epsilon}{N_1 + N_2} = \frac{\epsilon q e^{-\epsilon/kT}}{1 + q e^{-\epsilon/kT}},$$

and the additional specific heat C_{VS} due to this cause will be

$$C_{VS} = \epsilon \frac{dN_2}{dT} = q \frac{\epsilon^2}{kT^2} \frac{e^{-\epsilon/kT}}{(1+qe^{-\epsilon/kT})^2}$$

per molecule.

A plot of this additional specific heat is shown in the diagram. As for all additional specific heats due to energy
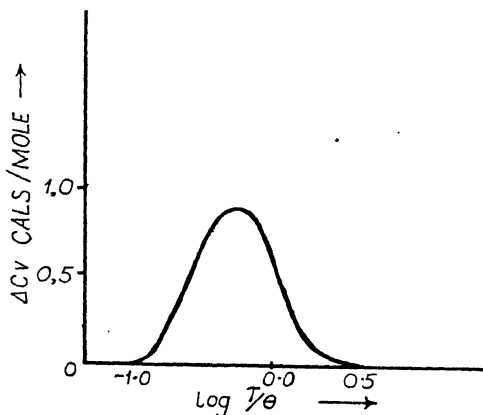
FIG. 6.

transitions in the solid, a maximum value of C_{VS} is observed in the neighbourhood of the characteristic temperature $\Theta \simeq \epsilon/k$ and C_{VS} falls off to zero either above or below this temperature.

Direct integration or an *a priori* calculation shows that the maximum contribution of such an effect to the energy content E and heat content H is simply $Nq\epsilon/(1+q)$ per gramme molecule, since when $T \gg \Theta$

$$N_2 = qN_1.$$

When such transitions take place at temperatures below the lowest at which measurements of the specific heat have been made, the value of the heat content as calculated from specific-heat measurements will be too low by

$$Nq\epsilon/(1+q).$$

This would mean, however, that the characteristic temperature $\Theta = \epsilon/k$ is considerably below the lowest temperature of measurement, and consequently that ϵ is very small. In consequence (cf. p. 13) no serious error can arise from this cause in the evaluation of heat contents.

Quite a different situation arises for other thermodynamic functions such as the entropy. The additional entropy due to the Schottky effect may be calculated from the integral

$$\Delta S = \int C_{VS} \, d \ln T,$$

and if the integration is performed from 0 to ∞ (in practice this simply means over the range of temperatures where C_{VS} is appreciable, cf. p. 71), this integral has the finite value

$$\Delta S = R \ln(q+1).$$

However small the value of ϵ separating the two states, and, consequently, however low the temperature at which the transition takes place, if the effect has been missed through not carrying specific-heat measurements to sufficiently low temperatures, the calculated value of the entropy from heat data will be too low by

$$R \ln 2, \, R \ln 3, \, ..., \text{etc.,}$$

according as $\quad q = 1, 2, ..., \text{etc.}$

This calculation of the simplest type of transition in a solid may be compared with experiment in two ways. The additional specific heat will be superimposed on the normal curve due to the lattice vibrations. For cubical lattices the normal curve fits a Debye function with constant Θ with sufficient accuracy to permit a calculation of C_{VS} from the experimental data, with the following results:

Substance	ϵ cals. (per mole)	Θ (Schottky)	Θ (Debye)
Diamond	2,120	1,070	1,840
Silicon	490	246	..
Grey tin	137	69	..
Lithium	407	205	..
Sodium	189	95	159
Potassium	117	59	99·5

An additional check on the theory is that since this transition leads to no volume change (there being no effect on the neighbouring atoms when any one atom changes its energy state), the coefficient of expansion follows Gruneisen's rule,

$$\frac{dV}{dT} = YK_0 C_V,$$

where C_V is the Debye specific heat obtained after subtracting C_{VS} from the experimental value; K_0 is the compressibility.

The soundness of using the theoretical Debye curve to compute an anomaly has been questioned,[†] but at temperatures where the Debye specific heat is small in any case, no serious error seems likely to arise. Thus crystalline gadolinium sulphate. (cf. p. 89) shows a Schottky effect; the specific heat of the solid obeys the T^3 law down to 7° K., but below this temperature the specific-heat curve begins to turn upwards till at 1·6° K. the specific heat is 500 times the value to be expected from the T^3 law.

In this case a satisfactory physical explanation is available for the energy changes occurring. The Ga^{+++} ion is in an $^8S_{7/2}$ state, i.e. it has an eightfold degeneracy in the absence of superposed electric and magnetic fields. Interaction with the non-uniform electrostatic field of the crystal lattice removes the degeneracy. This means that the eight levels have slightly different energies, $\Delta E \simeq 0 \cdot 52$ cal./mole. In consequence the higher levels are progressively emptied in the neighbourhood of the temperature given by $RT = 0 \cdot 52$ cal. Solid (ortho-para) hydrogen (cf. p. 106) shows a similar effect in the specific heat; the effect corresponds with the presence of three different energy levels ($\Delta E \simeq 7 \cdot 5$ cals.) in the solid.

From the standpoint of thermodynamics, more important examples of such effects arise when the transition takes place below the lowest temperature of measurement, and lead to an apparent departure from the heat theorem. The following

[†] Cf. Fowler, Bakerian Lecture 1935, *Proc. Roy. Soc.* **151** A, 1.

table† gives the difference between the entropy for a number of gases calculated from vapour-pressure curves or chemical equilibria, and calculated from the integral

$$\int C_P \, d\ln T,$$

assuming the heat theorem applies to the solidified gas.

Gas	Difference per mole	Notes
N_2	$-0\cdot07 \pm 0\cdot20$	Within experimental error.
CO_2	$0\cdot32 \pm 0\cdot27$	Dubious.
CO	$\left.\begin{array}{c} 1\cdot06 \pm 0\cdot25 \\ 1\cdot12 \pm 0\cdot10 \end{array}\right\}$	Two different observers.
N_2O	$0\cdot90 \pm 0\cdot32$	
NO	$0\cdot75 \pm 0\cdot10$	

To appreciate the significance of this table it should be noted that $R\ln 2 = 1\cdot4$ approx., and that a positive difference in the second column indicates that in computing entropy from heat data some contribution has been neglected (cf. p. 28), leading to an apparent departure from the heat theorem of the expected order of magnitude. The results suggest that the molecules CO, N_2O, NO undergo some energy transition in the solid below the lowest temperature of measurement. In view of the fact that the atoms in any of these molecules are very similar, but not identical, it has been suggested that the molecules take up random positions such as CO, OC in the crystal at ordinary temperatures. At very low temperatures the energy difference between an arrangement such as

$$\begin{array}{cccc} C\!-\!O & C\!-\!O & C\!-\!O & C\!-\!O \\ C\!-\!O & C\!-\!O & C\!-\!O & C\!-\!O \\ C\!-\!O & C\!-\!O & C\!-\!O & C\!-\!O \end{array}$$
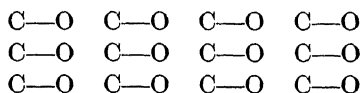
and a random arrangement, e.g.

$$\begin{array}{cccc} CO & OC & CO & CO \\ OC & OC & OC & CO \\ CO & CO & CO & OC \end{array}$$
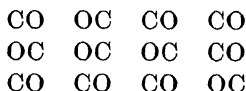
† Clusius, *Nature*, **132**, 775 (1932).

is comparable with kT and leads to a transition to the lowest state, with corresponding entropy and energy decrease.

The ammonium-chloride effect

When the transition into a higher energy level is *not* independent of the neighbouring atoms, complications arise
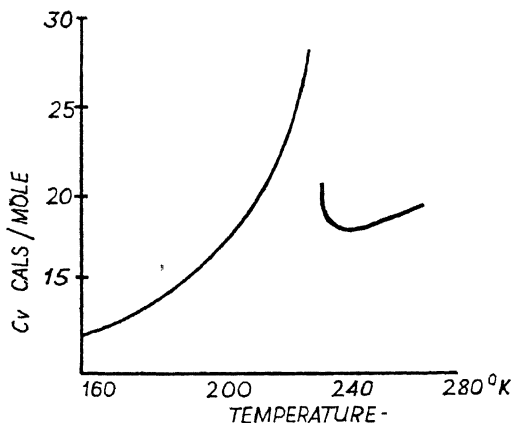
FIG. 7.

which make exact statistical calculation difficult. This is due to the fact that the energy difference between two states depends on the number of molecules already in the higher state. Furthermore, owing to the altered interaction between neighbours, the transition is accompanied by a change in volume and a change in the infra-red absorption of the crystal.

The diagram shows the additional specific heat superimposed on the normal curve in such a case. Such effects are shown by most ammonium salts in the neighbourhood of $230°$ K. and by other substances such as FeO ($185°$ K.), Fe_3O_4 ($115°$ K.), MnO ($116°$ K.), MnO_2 ($93°$ K.), n-butyric acid ($221°$ K.), HBr ($88°$ K.), HI ($70°$ K. and $120°$ K.), CH_4 ($20°$ K.), and also by hydrides such as SiH_4, HF, PH_3, H_2S, but not H_2O.†

† Landolt Bornstein, *Tabellen*, 5th ed.

One explanation (cf. Fowler, l.c.) which seems particularly applicable to hydrogen compounds is that below the transition temperature the asymmetric ions are oriented in the crystal, but that when they acquire more kinetic energy of oscillation than the maximum energy of mutual orientation, they begin to rotate freely in the lattice. It is clear that the orienting force on an ion surrounded by neighbours already rotating is smaller than when these were themselves oriented, which explains why the energy of transition depends on the number already in the higher state. The specific-heat anomaly of such interactions is much steeper than for the Schottky effect.

In support of the view that the transition involved is a change from orientation in the lattice to free rotation is the increased symmetry of the crystal above the transition point. The volume change is likewise due to a decreased interaction between the ions. Furthermore, the hypothesis is supported by the fact that the different ammonium salts show the effect at approximately the same temperature; other substances show transitions at temperatures which are lower the more symmetrical the molecule, and H_2O, which is strongly coordinated, does not show the effect, whereas H_2S does. At the same time any change of transition energy, due to the effect of atoms already in the state of higher energy, will give similar specific-heat curves. Examples are the change from ferromagnetism to paramagnetism, or from an ordered to a disordered alloy, discussed below. The physical change in the oxides of the transitional elements has not yet been elucidated, but is unlikely to be some form of free rotation replacing mutual orientation of the atoms.

The effect of such specific-heat anomalies on the thermodynamic functions is similar to that of Schottky transitions, but not so amenable to calculation.

General theory of specific heats in the neighbourhood of transition points

From the standpoint of formal thermodynamics a transition point in a substance which is connected with a change of state may be represented as the intersection of the free-energy curves of the two states. A well-known transition is
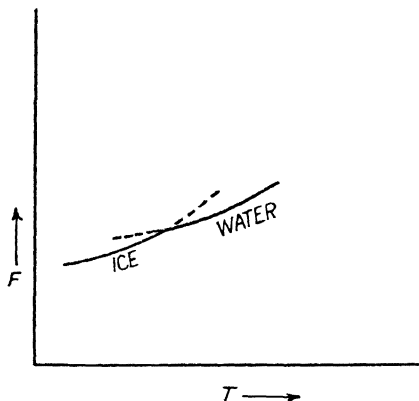
Fig. 8.

the case of melting. The diagram shows an intersection of the F, P, T surfaces for ice and water by the F, T plane corresponding with $P = 1$ atmosphere.

The state of lower free energy is the stable form, and since the curves intersect at $0.0°$ C. there is a spontaneous transition at this point from ice to water.

Although the free energies per unit mass (or per mole if the same molar unit is used in the two phases) are the same at this equilibrium point, the heat contents and entropies in the two states are not the same, so that the transition from ice to water is accompanied by an absorption of heat, a so-called latent heat.

Even in the case of melting this formal treatment of a transition point is not wholly adequate, as is shown by

experiments on the specific heat of ice just below the melting-point.† Fig. 9 shows the sharp rise observed, though the range of temperatures over which it takes place becomes narrower as the ice is progressively purified. This rise resembles the ammonium-chloride effect, but its statistical
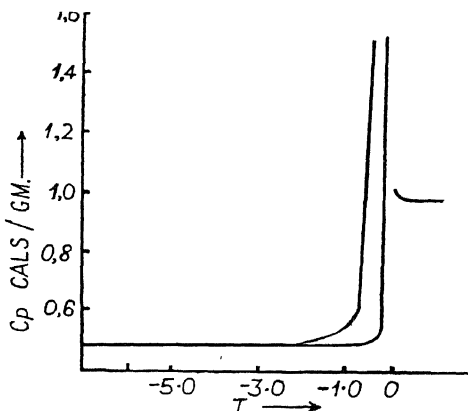
FIG. 9.

interpretation is not the same, since allowance must be made for the effect of impurities.

If ΔT_m is the total lowering of the melting-point due to an impurity of concentration C_0, and if no solid solutions are formed, a lowering ΔT when fraction X is molten will correspond to a solution of concentration C_0/X. If Raoult's law is obeyed, ΔT is proportional to the concentration of impurity, and

$$\frac{\Delta T}{\Delta T_m} = \frac{1}{X}.$$

If L is the latent heat of transformation, the heat used in partial melting is

$$Q = LX = L\frac{\Delta T_m}{\Delta T},$$

† Dickinson and Osborne, *Bull. Bur. Stand.* **12,** 69 (1915).

and the anomalous specific heat below the melting-point due to the presence of an impurity is

$$\Delta C_V = \frac{dQ}{dT} = \frac{\Delta T_m}{\Delta T^2} L, \quad \text{since} \quad \frac{d\Delta T}{dT} = 1.$$

This simple expression agrees with the observation that the specific-heat curves become steeper as the ice is purified, and experiment leaves it undecided how sharp the transition from a really pure solid to a liquid can be. A rise of specific heat before the actual melting-point would involve an abnormally rapid change of slope of the F, P, T surfaces in the neighbourhood of the transition point, but as long as there is a latent heat these surfaces must intersect at an angle.

In addition to the phenomenon of melting a number of other transitions in the solid state are known which are only completed over a range of temperatures, such as the change ferromagnetism–paramagnetism or ordered–disordered alloy. Such changes could not be discussed in terms of free-energy surfaces without introducing an additional degree of freedom, such as the degree of spontaneous magnetization or of spontaneous order of the solid, and a statistical treatment is required for proper interpretation of the phenomena.

Disordered–ordered solid solutions.

Reference has already been made to the fact (p. 47) that mixtures apparently do not obey the heat theorem, but that certain solid solutions can decrease their entropy by ordering the atoms in the lattice. This effect has been observed for such alloys as brass, Fe_3Al, Cu_3Pd, Cu_3Pt, $CuAu$, etc. X-ray investigation shows that above a certain temperature both the pure metals and solid solutions have face-centred cubic crystal lattices. On cooling the alloys sufficiently slowly, a fresh 'superstructure' appears below a transition range of temperatures, indicating that a haphazard arrangement of atoms on points in the cubic lattice has been replaced by an

ordered arrangement in which all the atoms of one kind occupy corresponding positions, e.g. all the Cu atoms at the corners and the Au atoms at the centres of the faces. Ordering can also be followed from other changes in the physical properties. For example, the electrical resistance decreases when a superstructure is formed in solid solution.

From the standpoint of thermodynamics and statistics the process of ordering leads to a gain in energy, and tends to take place spontaneously on cooling. It is, however, opposed by the thermal motions of the atoms since it involves a decrease in entropy, and can therefore only become prominent at temperatures where the gain in energy on ordering is large compared with the average thermal energy of the atoms. It is only for certain alloys that these temperatures are sufficiently high for the requisite migrations to take place in a measurable interval of time.

A simple formal treatment has been given by Bragg and Williams.† It is first necessary to define the degree of order in a solid solution. This can be done in a number of ways, one of which involves the idea of 'replacements'. Starting with a cubic lattice composed entirely of B atoms, the solid solution involves the replacement of a certain number n of these by A atoms. If a fraction r of the replacements occur in the positions required by a superstructure for A atoms, there will be nr positions of order α and $n(1-r)$ positions of disorder β.

The degree of order S is defined as follows: If p is the probability that an α position is occupied by a replacement of A for B,

$$S = \frac{p-r}{1-r},$$

i.e. when $p = 1$, $S = 1$ (complete order),

$p = r$, $S = 0$ (complete disorder).

The increase in potential energy at constant temperature

† *Proc. Roy. Soc.* **145** A, 699 (1934).

when a replacement is moved from a β to an α position will be $V = V(S, T)$, a function of the number of A atoms already in α positions.

The distribution of atoms corresponds with nr $(B \to A)$ replacements among n sites, there being nr positions α of order. At any moment the number of α positions available is

$$nr - pnr,$$

and the number of β positions available is

$$n(1-r) - (1-p)nr,$$

so that applying Boltzmann's expression

$$\frac{p}{1-p} = \frac{r(1-p)}{(1-2r+pr)} \, e^{V/kT}.$$

If $r = \frac{1}{2}$, e.g. for Fe_3Al, for which only the cube centres are positions of order, and $x = V/kT$,

$$S = \tanh\tfrac{1}{4}x.$$

In order to obtain a quantitative solution, V is assumed proportional to the degree of order,

$$V = V_0 S,$$

to allow for the interaction of the neighbours, but is assumed independent of temperature for simplicity, since there is no great expansion of the lattice over the range of temperatures considered.

The degree of order at equilibrium S_e will be given by the intersection of the curves $V = V_0 S$, and

$$S = \tanh V/kT,$$

i.e.
$$S_e = \tanh \frac{S_e V_0}{kT}.$$

This equation gives a rapid increase of S_e in the neighbourhood of a critical temperature

$$T_C = \frac{V_0}{4k}$$

above which $S_e \simeq 0$. For Fe_3Al

$$T_C = 833° \, \text{K.,} \qquad V_0 = 0\cdot29 \text{ volts.}$$

The energy changes accompanying changes in S_e may be estimated as follows:

$$dp = (1-r)\, dS,$$

$$dE = Vnr\, dp = V_0\, S\, nr(1-r)\, dS,$$

and just below the critical temperature an approximation for S_e is

$$S_e^2 = 3(T_C - T)/T_C.$$

Differentiating, $\qquad 2S_e\, dS_e = -\dfrac{3\, dT}{T_C}$

Substituting for dS from the above equations,

$$\frac{dE}{dT} = \Delta C_V = 6nrk(1-r).$$

The maximum, for $r = \frac{1}{2}$, of $r(1-r)$ gives $\Delta C_{V\,\mathrm{max}} = \frac{3}{2}nk$. For Fe_3Al there are in all $n = \frac{1}{4}N$ replacements per N atoms of both metals, so that the anomalous specific heat may rise to as much as $\frac{1}{8}$ of the Dulong and Petit value for the lattice vibrations. More detailed treatment shows that the dissipation of order above T_C is less rapid than is indicated by the simple treatment just given, so that ΔC_V falls off more slowly above T_C than is indicated.

Paramagnetism and ferromagnetism

The statistical treatment of paramagnetism is discussed in the following chapter. Paramagnetic solids usually obey the Weiss-Curie law, according to which the susceptibility

$$X = C/(T + \Delta),$$

where C and Δ are constants. At temperatures where T becomes of the same order as Δ, X is no longer independent of the field strength $\mathfrak{H}$, and Curie's law ceases to hold. Both C_V and the change in heat content on magnetization become abnormally large near the Curie point, below which the solid becomes ferromagnetic. Typical Curie points are $755°$ C. for iron, $588°$ C. for magnetite, $376°$ C. for nickel, though for weakly ferromagnetic substances the Curie point is not

observed till much lower temperatures. When cooling curves are plotted for paramagnetic substances, a change of slope is observed in the neighbourhood of the Curie point, owing to the change in C_V, but there is no arrest corresponding with the evolution of latent heat at a fixed temperature.

In the absence of a strictly quantitative theory of ferromagnetism, a formal thermodynamic treatment may be given as follows. If $\mathfrak{H}$ is the magnetic field and I the intensity of magnetization, the work done on the substance in producing this magnetization is $\int \mathfrak{H}\, dI$ and the heat content may be defined as

$$H = E + PV - \mathfrak{H}I.$$

If $[E+PV]$ is independent of the state of magnetization, then taking $\mathfrak{H}$ and T as independent variables,

$$\left(\frac{\partial S}{\partial \mathfrak{H}}\right)_{P,T} = \left(\frac{\partial I}{\partial T}\right)_{P,\mathfrak{H}},$$

whence the entropy change on magnetization is

$$\Delta S = \int_{\cdot}^{\mathfrak{H}_2} \left(\frac{\partial I}{\partial T}\right)_{P,\mathfrak{H}} d\mathfrak{H}.$$

For paramagnetic substances $I = X\mathfrak{H}$, and if the substance obeys Curie's law, $X = C/T$, so that

$$\left(\frac{\partial I}{\partial T}\right)_{P,\mathfrak{H}} = -\frac{C\mathfrak{H}}{T^2},$$

which is only appreciable at low temperatures,

$$\Delta S = -\frac{\mathfrak{H}^2 C}{2T^2},$$

and the additional specific heat of paramagnetic substances is

$$\Delta C_V = T d\left(\frac{\Delta S}{\partial T}\right)_V = \frac{\mathfrak{H}^2 C}{T^2}.$$

Ferromagnetics.

Ferromagnetic substances below the Curie point show a spontaneous magnetization even for $\mathfrak{H} = 0$.

If I_S is the saturation magnetization, the inner field, following Weiss, may be written

$$H_m = A I_S,$$

where A is a constant, and the energy of magnetization

$$E_m = \tfrac{1}{2} A I_S^2$$

per unit volume, or $\tfrac{1}{2}(A/\rho)I_S^2$ per gramme.
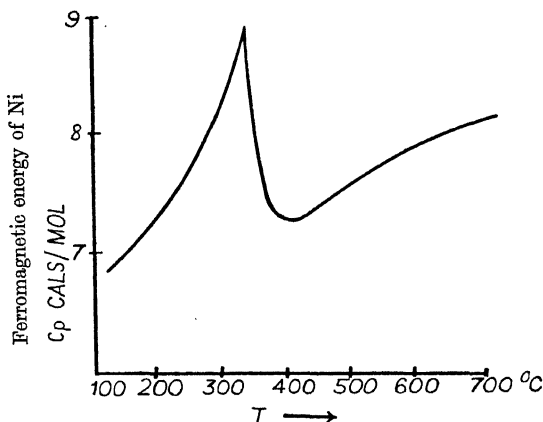
FIG. 10.

The additional energy of spontaneous magnetization leads to an additional specific heat

$$\Delta C_{Vm} = \frac{\partial E_m}{\partial T} = - \frac{A}{\rho} I_S \frac{dI_S}{dT}.$$

Both experiment and theory show that $\dfrac{dI_S}{dT}$ is largest near the Curie point, so that the maximum contribution to the specific heat is in this neighbourhood, and is in general bigger where I_S is still large. Thus the maximum value of ΔC_{Vm} is observed at the Curie point, but ΔC_{Vm} falls off more slowly on the low-temperature side of the maximum.

Fig. 10 shows the addition to the normal specific heat near the Curie point of nickel.

THE ATTAINMENT OF VERY LOW TEMPERATURES

THE energy changes of atoms in a solid are in general characterized by the interaction of neighbours. In phenomena such as ferromagnetism, ordered alloys, or transformations of the ammonium-chloride type this interaction makes it difficult to give a quantitative calculation of the energy changes involved. The paramagnetism of many solids only shows evidence of such interaction of neighbours at very low temperatures, and this makes magnetic methods of cooling of great importance.

Unattainability of the absolute zero.

Before discussing the methods which have been used for attaining very low temperatures it is useful to appreciate the significance of a theorem of Nernst's, which states that the absolute zero is unattainable by any reversible process in finite dimensions.

This can be demonstrated from a Carnot cycle. At a temperature ΔT above 0°K. the change $A \to B$ is carried out reversibly and isothermally:

$$\Delta S_{A \to B} = \frac{F - H}{\Delta T}$$

The system is then cooled adiabatically to 0°K., in which process $\Delta S = 0$, and the reverse process $B \to A$ carried out at absolute zero requires entropy change $\Delta S = 0$ from the Nernst Heat Theorem. Finally the system is heated adiabatically to ΔT.

If such a cycle were possible, a spontaneous entropy decrease $\Delta S_{A \to B}$ could be produced at ΔT without any other change, e.g. in the working substance. Since this is contrary to the second law, the conclusion is that if the heat theorem holds it must be impossible to cool a working substance

adiabatically to absolute zero, i.e. the absolute zero is unattainable.

Inspection of the equations

$$\Delta S = C_V \frac{\Delta T}{T} = \frac{\Delta Q}{T}$$

shows that this theorem is in a sense trivial. Provided reversible processes are available which give appreciable entropy changes down to the lowest temperatures, it is always possible to produce quite large changes of $\Delta T/T$, since C_V is very small. From the thermodynamic aspect the change from $0\cdot1$ to $0\cdot001°$ K. is as important as the change from $100°$ K. to $1°$ K., since it is the ratio $\Delta T/T$ that matters. It is always possible to attain temperatures which appear to be very small numerically, but the theorem of the unattainability of the absolute zero automatically comes into force when no further entropy changes can be found, so that the ratio $\Delta T/T$ which measures the cooling cannot be increased further.

Magnetic processes of cooling.

Every substance has a diamagnetic susceptibility independent of temperature. This can be shown in an elementary way by considering the electrons in closed orbits as equivalent to electric currents, which set themselves so as to oppose the action of an applied magnetic field. The atoms of a limited number of substances have in addition permanent magnetic moments, due to uncompensated spin or orbital magnetism, and such substances have a paramagnetic susceptibility dependent on temperature.

Methods of cooling depending on the liquefaction of gases, i.e. on the entropy change on vaporization, begin to fail when the vapour pressure of the gas becomes so small that it becomes technically impossible to produce a sufficient entropy change in a finite time. The conditions under which the paramagnetic susceptibility of solids can then be used

for producing entropy changes down to very low temperatures will be clear from the following discussion.

The change in entropy on magnetization is

$$\Delta S = \int_{\mathfrak{H}_1}^{\mathfrak{H}_2} \left(\frac{\partial I}{\partial T}\right)_{P,\mathfrak{H}} d\mathfrak{H} \quad \text{(cf. p. 83)}$$

and the heat evolved is $T\Delta S$.

In the magnetic method of cooling the paramagnetic substance is magnetized, and the heat evolved is absorbed by the surroundings, using helium as a transport gas and liquid hydrogen to absorb the heat evolved. When temperature equilibrium has been reached, the helium is pumped off, and on removing the magnetic field a corresponding entropy increase must take place in the working substance, causing absorption of heat and a fall in temperature.

In order that the working substance may give large entropy changes down to the lowest available temperatures it must have $\frac{\partial I}{\partial T}$ large. Since $I = X\mathfrak{H}$, where X is the susceptibility, and since most paramagnetic substances obey the Weiss-Curie law
$$X(T+\Delta) = C,$$

$$\frac{\partial I}{\partial T} \quad -\frac{\mathfrak{H}C}{(T+\Delta)^2}, \qquad \Delta S = -\frac{\mathfrak{H}^2 C}{2(T+\Delta)^2}.$$

It is clear that the entropy change on magnetization will only increase with falling temperature so long as $T \gg \Delta$, so that a suitable working substance must have Δ as small as possible.

Statistical deduction of the Curie law, and significance of Δ.

The statistical deduction of Curie's law for the paramagnetic susceptibility of solids is based on the assumption that the solid contains elementary magnets which tend to orient themselves parallel to an applied magnetic field, but which are prevented from a complete parallelism by the

thermal motions of the atoms. If the elementary magnets have moments μ, their potential energy when they are inclined at an angle θ to the applied field $\mathfrak{H}$ is $-\mathfrak{H}\mu \cos \theta$ if there is no interaction between neighbours. According to Boltzmann's theorem, the number of molecules falling in a solid angle

$$d\Omega = d(\cos \theta)\, d\phi$$

with their axes inclined at θ to the field will be proportional to

$$e^{\mu \mathfrak{H} \cos \theta / kT}\, d\Omega,$$

and the resulting susceptibility will be

$$\mu \cos \theta \text{ per atom.}$$

The *average* magnetic susceptibility per atom will be

$$\bar{\mu} = \frac{\sum e^{\mu \mathfrak{H} \cos \theta / kT}\, d\Omega\, \mu \cos \theta}{\sum e^{\mu \mathfrak{H} \cos \theta / kT}\, d\Omega}.$$

It should be noted that this quantity is obtainable more compactly in terms of the partition function

$$Z = \sum e^{\mu \mathfrak{H} \cos \theta / kT}\, d\Omega,$$

since the potential energy $\bar{e}$ per atom in a magnetic field is $\bar{e} = -\mathfrak{H}\bar{\mu}$ and since $\bar{e} = -\partial \log Z / \partial(1/kT) = -\mathfrak{H}\bar{\mu}$.

According to the quantum theory, only definite values of $\cos \theta$ can be assumed by the magnetic moments. Except at very low temperatures or very large values of $\mathfrak{H}$, the average susceptibility per atom is the same if classical statistics is used, i.e. if the summation is replaced by an integration. If there are n atoms per unit volume, the susceptibility X per unit volume may therefore be written

$$X = n \left[\frac{\int \int e^{\mu \mathfrak{H} \cos \theta / kT} \mu \cos \theta \sin \theta\; d\theta d\phi}{\int \int e^{\mu \mathfrak{H} \cos \theta / kT} \sin \theta\; d\theta d\phi} \right].$$

Writing

$$x = \frac{\mathfrak{H}\mu}{kT}.$$

This reduces to
$$X = n\mu \left[\coth x + \frac{1}{x} \right],$$

and for small values of x gives the Curie law:

$$X = \frac{n\mu^2}{3kT}.$$

Before comparison with experiment the small diamagnetism of the solid must be allowed for.

The Weiss correction only becomes appreciable when $T \simeq \Delta$, and is due to the electrical and magnetic interaction of the elementary magnets with their neighbours. Suitable working substances for which Δ is very small are gadolinium sulphate $Gd_2(SO_4)_3 8H_2O$, iron ammonium alum

$$Fe_2(SO_4)_3(NH_4)_2SO_4 24H_2O,$$

and similar salts of the rare earths and the transitional elements. The interactions between neighbours are small in such cases because the electron orbits responsible for paramagnetism are deeply 'buried' in the molecule, and are surrounded by a very symmetrical electrical field from the neighbouring ions, owing to the large number of water molecules.

From the thermodynamic point of view, it is interesting to discuss the source of the entropy of magnetization. In gadolinium sulphate the magnetic quantum number of the gadolinium ion is $j = \frac{7}{2}$, and in a very weak field the orbits of the electrons can take up angles given by

$$\cos\theta = j/j, \qquad (j-1)/j, \qquad (j-2)/j, \qquad (j-3)/j$$

with respect to the field. Allowing for the difference between clockwise and counter-clockwise spins, this gives $4 \times 2 = 8$ positions. The magnetic moment per gramme atom is $gj\beta$, where β, the Bohr magneton, $= \frac{Nek}{4\pi m} = 5{,}567$ units, and $g = 2$ is the ratio of the mechanical to the magnetic moment of the electron.

The work required to set the orbits parallel to the field is thus $gj\beta\mathfrak{H}(1-\cos\theta)$. If the salt is in the earth's field only, this work is very small, and comparable with RT only below

$10^{-5}\,^{\circ}$K. Neglecting the electrical orienting forces, thermal agitation would lead to all states being equally occupied down to this temperature. (Electrical forces raise it to about 1°K.) If the specific heat could be measured down to this temperature, an anomaly would be observed whose integral $\int C_V\,d\ln T = -R\ln 8$. This is missed in the ordinary experimental evaluation of entropy (cf. p. 28) since the temperatures are not carried low enough. In a strong magnetic field, on the other hand, the energy gain on setting the molecules parallel to the field becomes greater than RT, so that all positions are no longer equally filled. As a corollary, the entropy defect is now less than $R\ln 8$, the difference appearing as entropy of magnetization. This has thus a maximum value which cannot be exceeded, a result which is connected with the fact that the susceptibility begins to fall off as the solid reaches magnetic saturation (cf. p. 88), so that the integral

$$\Delta S_{\text{magnetization}} = \int_{\mathfrak{H}_1}^{\infty} \left(\frac{\partial I}{\partial T}\right)_{P,\,\mathfrak{H}} d\mathfrak{H}$$

has a finite value.

THE GASEOUS STATE

WHEREAS progress in the thermodynamics of the solid state depends on the correct use of the heat theorem, the thermodynamic functions of gases have only become amenable to calculation by a systematic use of the theory of the partition function, together with energy levels deduced from band spectra. This is due to the fact that the experimental evaluation of even heat contents of gases at high temperatures is not an easy problem.

The translational energy of gas molecules.

The theory of the partition of translational energy among gas molecules is chiefly of importance in providing a theoretical expression for the entropy constant of a gas. At ordinary temperatures where the equipartition of energy holds among the molecules, the translational specific heat of a perfect gas is $C_P = \frac{5}{2}R$ per mole, and the entropy is

$$S = R \ln \frac{T^{\frac{5}{2}}}{P} \mathfrak{A},$$

where $\mathfrak{A}$ is the entropy constant.

If gases obey the heat theorem, i.e. have $S = 0$ at $0°$ K., the translational specific heat must fall off at very low temperatures. This phenomenon, which is called the degeneracy of gases, is very difficult to observe experimentally owing to the simultaneous importance of the van der Waals correction at low temperatures and high densities, at which degeneracy would be observable.

Note on the van der Waals correction.

From the experimental standpoint, when a gas shows considerable departures from the gas laws the results can be compactly summarized in terms of the fugacity function

This is defined to be such that the change in free energy on compressing a gas is accurately given by the equation

$$\Delta F = RT \ln f_1/f_2,$$

where f_1, f_2 are the fugacities at P_1 and P_2 respectively.

The correction to the value of ΔF which would be obtained if the gas laws held is thus

$$A_P = RT \ln P_1/P_2 - RT \ln f_1/f_2.$$

In the limit at very low densities the gas laws are obeyed, and $f_2 = P_2$, so that the correction A_P at any finite pressure is given by

$$A_P = RT \ln P - RT \ln f = RT \ln P/f.$$

Writing as the next approximation to the equation of state of a gas

$$V = \frac{RT}{P} - \alpha,$$

$$RT \ln f/f' = RT \ln P/P' - \alpha(P - P'),$$

and in the limit $(f' = P' \to 0)$

$$RT \ln f = RT \ln P - \alpha P, \quad \text{i.e.} \quad A_P = \alpha P.$$

Statistical calculation of degeneracy. ·

Although direct experimental observations are unsatisfactory, a theoretical calculation of degeneracy is possible on the basis of statistical theory.

For the case of the most probable partition of energy among particles, two auxiliary conditions must always hold, viz.

Constant total number of particles whatever the distribution:

$$\sum n_r = N.$$

Constant total energy: $\quad \sum n_r \epsilon_r = E.$

In order to define the energy states more closely, the molecules can be considered as located in a six-dimensional space by their coordinates, characterizing their distances from the origin, x_1, x_2, x_3, measured along three axes at right angles, and the projections of their momenta, p_1, p_2, p_3, along

these axes. Any molecule whose coordinates lie between x_1 and $x_1+\Delta x_1$, etc., lies in a cell of volume

$$\Delta x_1 \Delta x_2 \Delta x_3 \Delta p_1 \Delta p_2 \Delta p_3.$$

According to any form of quantum statistics, these cells must have a minimum size h^3, since by the uncertainty principle $\Delta p \Delta x \geqslant h$. From this restriction it is possible to calculate the number of cells corresponding to energies between ϵ and $\epsilon+\delta\epsilon$. The volume of such a six-dimensional phase space is

$$\int\int\int\int\int\int dx_1\,dx_2\,dx_3\,dp_1\,dp_2\,dp_3,$$

and is limited by the fact that no molecule can lie outside the physically available gas volume v, so that

$$v = \int\int\int dx_1\,dx_2\,dx_3,$$

and no molecule can possess energy greater than ϵ if it is to lie within the phase space up to ϵ, i.e.

$$2m\epsilon \geqslant p_1^2+p_2^2+p_3^2.$$

This is the equation of a sphere of total volume

$$V = \frac{4\pi}{3}(2m\epsilon)^{\frac{3}{2}}(\ \ \ )$$

which is the volume available from $\epsilon = 0$ to $\epsilon = \epsilon$. The volume available between ϵ and $\epsilon+\delta\epsilon$ is

$$dV = 2\pi v(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}\delta\epsilon.$$

Since the minimum volume of any cell is h^3, the number of cells a_r lying between ϵ_r and $\epsilon_r+\delta\epsilon_r$, amongst which the molecules with this energy can be distributed, is

$$a_r = \frac{dV}{h^3} = 2\pi v\frac{(2m)^{\frac{3}{2}}}{h^3}\epsilon^{\frac{1}{2}}\delta\epsilon.$$

In classical statistics identical molecules are considered as distinguishable objects, for the purpose of counting the number of possible distributions, irrespective of whether they are in the same cell or not. The number of ways of

distributing the N_r molecules in cells, n_1 in the first, n_2 in the second, and so on, is

$$\frac{N!}{n_1!\,n_2!\dots},$$

as has already been stated.

Einstein-Bose or Fermi-Dirac statistics for degenerate gases both take into account a further limitation on the number of possible distributions of n_r molecules of energy ϵ_r between the a_r cells.

According to the Einstein-Bose statistics, identical molecules can only be distinguished from one another if they are in different cells. The term 'degenerate', as in other cases, refers to the fact that it is impossible to distinguish two molecules of the same structure in the same cell.

The number of distributions of n_r molecules in the a_r cells lying between ϵ_r and $\epsilon_r + \delta\epsilon_r$ in this case will be

$$\frac{(n_r + a_r - 1)!}{n_r!\,(a_r - 1)!}.$$

This formula can be established in a number of ways. One of these, due to Brillouin, is as follows:

Instead of considering the Einstein-Bose gas, consider the number of permutations of n_r identical objects among $a_r - 1$ boxes, to be calculated as follows: The n_r objects and $a_r - 1$ boxes are thrown haphazard along a line, giving $(n_r + a_r - 1)!$ permutations, or allowing for the fact that the n_r objects are indistinguishable *per se*,

$$(n_r + a_r - 1)!/n_r!$$

permutations in all. The last box is now added at the end of the line, and the molecules to the left of every box, and between it and its neighbour, are piled into it, leaving an arrangement of molecules in boxes which has

$$(n_r + a_r - 1)!/n_r!$$

permutations. This arrangement is clearly identical with the Einstein-Bose case, except that the order of the boxes along the line has no significance for statistics. When account is

taken of this order along the line, there are $(a_r-1)!$ permutations of the a_r-1 boxes among themselves. The number of permutations of statistical significance is therefore

$$\frac{(n_r+a_r-1)!}{n_r!\,(a_r-1)!},$$

which is the required formula.

This gives the number of ways of distributing the n_r molecules in the a_r cells with energies between ϵ_r and $\epsilon_r+\delta\epsilon_r$. The total probability of an arrangement with n_1 molecules of energies between ϵ_1 and $\epsilon_1+\delta\epsilon_1$, n_2 molecules with energies between ϵ_2 and $\epsilon_2+\delta\epsilon_2$, and so on, is the continued product for all values of r:

$$W_{n,r} = \prod\left(\frac{(n_r+a_r-1)!}{n_r!\,(a_r-1)!}\right).$$

The maximum of W or $\log W$ gives the most probable distribution.

Using Stirling's theorem (p. 50) and neglecting unity compared with a_r,

$$\delta\log W_{\max} = 0$$
$$= \delta\left[\sum(n_r+a_r)\ln(n_r+a_r)-n_r\ln n_r-a_r\ln a_r\right].$$

As before, the two auxiliary conditions are (cf. p. 92)

$$\delta\sum n_r = 0, \qquad \delta\sum n_r\epsilon_r = 0,$$

and the distribution function in the Einstein-Bose statistics is

$$n_r = \frac{a_r}{Ce^{\mu\epsilon_r}-1},$$

where C and μ are constants to be determined as before by the physical values of

$$N = \sum n_r, \qquad E = \sum n_r\epsilon_r.$$

Fermi-Dirac statistics.

The distribution just quoted may be compared with the classic Maxwell-Boltzmann formula

$$n_r = \frac{a_r}{Ce^{\mu\epsilon_r}},$$

and with the distribution obtained in Fermi-Dirac statistics.

By analogy with Pauli's principle for individual atoms, the Fermi-Dirac statistics imposes the restriction on the distribution of n_r molecules among the a_r cells of energy ϵ_r that each of the a_r cells can contain one molecule or none, and not the very large number (up to n_r) as in the Einstein-Bose statistics. In view of this restriction, the number of distributions of n_r molecules in a_r cells is simply the number of combinations of a_r things taken n_r at a time, i.e.

$$\frac{a_r!}{n_r!\,(a_r-n_r)!},$$

and

$$W_{n,a} = \prod_r \left(\frac{a_r!}{n_r!\,(a_r-n_r)!}\right).$$

Applying the same methods as before, the most probable distribution with $\log W = $ maximum gives

$$n_r = a_r/(Ce^{\mu\epsilon_r}+1).$$

The entropy of a monatomic gas.

The above expressions at once give the complete values for the entropy and internal energy of a monatomic gas, since

$$N = \sum n_r, \qquad E = \sum n_r\,\epsilon_r,$$

and

$$S = k\ln W_{\max}.$$

For the Einstein-Bose statistics, substituting for n_r and replacing the summation by an integration, since the number of terms is very large,

$$N = A\int_0^\infty \frac{\epsilon^{\frac{1}{2}}\,d\epsilon}{(Ce^{\mu\epsilon}-1)}, \quad \text{where} \quad A = 2\pi v\left(\frac{2m}{h^2}\right)^{\frac{3}{2}},$$

$$S = R\ln C + E/T - A\int_0^\infty \epsilon^{\frac{1}{2}}\ln(1-e^{-\mu\epsilon}/C)\,d\epsilon,$$

$$E = A\int_0^\infty \frac{\epsilon^{\frac{3}{2}}\,d\epsilon}{(Ce^{\mu\epsilon}-1)}.$$

It may be noted that E is not quite the same as $\dfrac{\partial \ln Z}{\partial \mu}$ since the Boltzmann distribution does not apply.

The Fermi-Dirac statistics gives the similar expressions

$$N = A \int_0^\infty \epsilon^{\frac{1}{2}}/(Ce^{\mu\epsilon}+1)\, d\epsilon,$$

$$S = R \ln C + E/T + A \int_0^\infty \epsilon^{\frac{1}{2}}\ln(1+\epsilon^{-\mu\epsilon}/C)\, d\epsilon,$$

$$E = A \int_0^\infty \epsilon^{\frac{3}{2}}/(Ce^{\mu\epsilon}+1)\, d\epsilon.$$

Gas degeneracy will only become appreciable when these expressions differ notably from the Maxwell-Boltzmann distribution, i.e. when ± 1 becomes of the same order of magnitude as $Ce^{\mu\epsilon}$.

At temperatures sufficiently high to neglect ± 1, i.e. where there is no degeneracy, and the gas laws hold, it becomes possible to calculate the entropy constant of a perfect gas, without having to decide which form of quantum statistics it would obey at lower temperatures. Thus

$$N = (A/C) \int_0^\infty \epsilon^{\frac{1}{2}}e^{-\mu\epsilon}\, d\epsilon,$$

whence

$$C = \frac{v}{Nh^3}(2\pi mkT)^{\frac{3}{2}}$$

$$\frac{M^{\frac{3}{2}}T^{\frac{3}{2}}}{n} \times 3\cdot074 \times 10^{-4},$$

where n is the concentration in moles/litre, and M is the atomic weight of the particles.

Furthermore, where there is no degeneracy, i.e. $Ce^{\mu\epsilon} \gg 1$,

$$\ln\left(1+\frac{1}{Ce^{\mu\epsilon}}\right) \simeq \frac{e^{-\mu\epsilon}}{C},$$

$$S = R \ln C + E/T + (A/C) \int_0^\infty \epsilon^{\frac{1}{2}}e^{-\mu\epsilon}\, d\epsilon$$

$$= R \ln C + E/T + R = R(\tfrac{5}{2}+\ln C),$$

since for a monatomic perfect gas $E = \frac{3}{2}RT$. Substituting for C and writing $p = nRT$ for a perfect gas,

$$S = R\left[\tfrac{5}{2}\ln T - \ln p + \tfrac{5}{2} + \ln\frac{(2\pi mk)^{\frac{3}{2}}k}{h^3}\right],$$

from which the entropy constant is seen to be

$$\frac{S_0}{R} = \ln\frac{(2\pi mk)^{\frac{3}{2}}k}{h^3} + \tfrac{5}{2}.$$

Thermal data of a degenerate gas; the specific heat of metals.

The degeneracy of a gas becomes appreciable at temperatures where

$$C = \frac{M^{\frac{3}{2}}T^{\frac{3}{2}}}{n} \times 3{\cdot}074 \times 10^{-4}$$

becomes $\ll 1$. As has been stated, for all ordinary gases the van der Waals effects at the same temperature are so marked that a verification of the statistical theory becomes almost impossible. It is, however, possible to discuss a number of properties of metals in terms of the Fermi-Dirac statistics. The atomic weight of the electrons is only $M = 5{\cdot}43 \times 10^{-4}$. In problems of gaseous ionization (cf. p. 37) the electron gas is so dilute that the perfect gas laws apply, but the conduction electrons in metals are present at a much greater concentration. If every atom in the metal provides one conduction electron, the concentration n is of the order of 10^{-1} moles/c.c., and in view of the very small atomic weight $C \ll 1$ even at ordinary temperatures, making the electron gas in metals completely degenerate. The energy E of such a gas is given by the formula

$$E = E_0 + \alpha T^2,$$

where E_0, the zero-point energy per mole of the gas, is

$$E_0 = \frac{3}{40}\left(\frac{6N}{\pi v}\right)^{\frac{2}{3}}\frac{Nh^2}{m}$$

which for an electron gas is as much as 15 times the classical value $\frac{3}{2}RT$ at room temperatures. The conduction electrons

thus have very considerable mobility, but their contribution to the specific heat is only $C_{V_e} = \alpha T = \partial E/\partial T$, where

$$\alpha = 2\left(\frac{\pi v}{9n}\right)^{\frac{2}{3}} \frac{m}{\hbar^2} \pi^2 n k^2.$$

This would become comparable with the specific heat due to lattice vibrations at a sufficiently high temperature, but since these lattice vibrations become anharmonic at higher temperatures and also contribute a term $\Delta C_{V_{\text{lattice}}} = aT$ to the Dulong and Petit value, it is not always possible to obtain distinct evidence of the specific heat of the conduction electrons at high temperatures. At low temperatures, on the other hand, the value of C_V due to lattice vibrations falls off at a rate proportional to T^3, whereas the specific heat due to the conduction electrons only falls off proportional to T. It should therefore be possible to obtain evidence of the specific heat of the conduction electrons by investigating metals at very low temperatures. Although the treatment of the conduction electrons as a degenerate gas is not strictly accurate, since it neglects the effect of the positive ions of the metal lattice, the specific heats of metals such as Ag at very low temperatures show the expected T term (cf. p. 27).

THE THERMODYNAMICS OF HYDROGEN AND THE ROTATIONAL ENERGY OF GASES

THE distribution of rotational energy in a gas can be discussed in terms of the theory of the partition function and the energy levels deduced from band spectra. The thermodynamic functions of hydrogen and deuterium are, however, so dependent on a correct evaluation of the rotational energy that it is preferable to discuss these gases in detail before dealing with the special issues that arise for more complicated molecules.

According to the classical theory of equipartition of energy, each of the rotational degrees of freedom of a molecule makes a contribution $\frac{1}{2}R$ to the specific heat. For polyatomic molecules whose rotation can be described about three axes at right angles the rotational specific heat is thus $C_{\text{rot}} = \frac{3}{2}R$.

According to quantum theory, rotational energy is quantized in such a way that the energy of the rth rotational quantum according to the Schrödinger equation is

$$E_r = \frac{r(r+1)h^2}{8\pi^2 I}$$

where I is the moment of inertia of the molecule about the axis about which rotation is being considered. The moment of inertia of relatively light molecules such as

$$F_2 \quad 25 \cdot 3 \times 10^{-40} \text{ c.g.s.}, \qquad O_2 \quad 19 \cdot 5 \times 10^{-40} \text{ c.g.s.},$$
$$N_2 \quad 13 \cdot 8 \times 10^{-40} \text{ c.g.s.}$$

is, however, sufficiently large to make the quanta of rotational energy and the characteristic temperature

$$\Theta_{\text{rot}} = \frac{h^2}{8\pi^2 I k}$$

very small. Equipartition is therefore set up for the rotational energy of molecules, with two exceptions.

In the first place, diatomic molecules and linear poly-atomic molecules have a very small moment of inertia and very large rotational quantum about the line joining the atoms, so that this degree of freedom does not contribute to the rotational specific heat except at very high temperatures. Such molecules therefore have only two rotational degrees of freedom taking part in the equipartition, and $C_{\text{rot}} = R$.

For simple molecules the effect of rotational energy is to add the term $\dfrac{8\pi^2 I k}{h^2}\dfrac{g}{s}$ to the chemical constant (cf. p. 37), provided the temperatures are sufficiently low for the moment of inertia of the molecule to be constant. At higher temperatures the vibration of polyatomic molecules alters their linear dimensions, and moment of inertia, thus introducing a correction to the rotational energy which cannot be expressed in any simple form. The only satisfactory way to calculate the contribution of rotation to the thermodynamic functions when this happens is by using the individual energy levels as obtained from band spectra (cf. p. 115).

The thermodynamics of hydrogen

The moment of inertia of the hydrogen molecule is only 0.47×10^{-40} c.g.s. units, and this makes the quantum of rotational energy so large that departure from equipartition and a falling off from the rotational specific heat begins to be appreciable not much below room temperature, and below $50°$ K. hydrogen has zero rotational specific heat, thus behaving like a monatomic gas.

Although the magnitude of the rotational quantum was known, no satisfactory partition function giving a correct specific heat could at first be constructed. A diatomic molecule with rotational energy ϵ_r can have the rotational quanta distributed in $2r+1$ ways amongst its two axes (cf. p. 114),

and thus has a quantum weight $(2r+1)$. The partition function would thus appear to be

$$Z_{\text{rot}} = \sum_0^\infty (2r+1)e^{-\epsilon_r/kT},$$

where

$$\epsilon_r = \frac{r(r+1)h^2}{8\pi^2 I}.$$

Writing

$$\Theta = \frac{h^2}{8\pi^2 Ik}, \qquad \frac{\Theta}{T} = \sigma,$$

$$Z = \sum (2r+1)e^{-r(r+1)\sigma},$$

$$E_{\text{rot}} = -\frac{Nh^2}{8\pi^2 I}\frac{d\ln Z}{d\sigma} \text{ per mole},$$

$$C_{\text{rot}} = \frac{dE_{\text{rot}}}{dT} \text{ per mole} = \frac{dE_{\text{rot}}}{d\sigma}\frac{d\sigma}{dT}$$

$$= R\sigma^2\frac{d^2\ln Z}{d\sigma^2},$$

as is usual when the partition follows Boltzmann's theorem.

From the band spectrum of hydrogen,

$$I = 0.47 \times 10^{-40} \text{ c.g.s. units}$$

and

$$\sigma = \frac{85.90}{T}.$$

Like other thermodynamic quantities (e.g. the Schottky effect, p. 71) this expression for C_{rot} gives a decrease for C_{rot} at low temperatures, with a peak in the neighbourhood of the characteristic temperature $\Theta = 85.90°\,\text{K}$. This is quite unlike the experimental curve.

The discovery of ortho- and para-hydrogen has shown the discrepancy to be due to the assumption that all transitions between the rotational states are possible under ordinary experimental conditions.

If the nuclei have a spin, i.e. a magnetic moment with a definite direction in space, it is possible in symmetrical diatomic molecules (cf. also p. 118) to distinguish between molecules with spins parallel (ortho) and antiparallel (para).

From Schrödinger's equation and an extension of Pauli's principle it follows that unexcited H_2 molecules can only exist in the following states:

Antisymm. Proper function.	*Symm. Proper function.*
Nucl. Spins Parallel	Nucl. Spins Antiparallel
Ortho	Para
Odd Rot. States 1, 3, 5	Even Rot. States 0, 2, 4

The quantum weight of the ortho state is three times that of the para state. It was first suggested by Dennison that if the transition H_2 ortho $\rightarrow$ para was infrequent during an ordinary specific-heat determination, the correct energy function to use is not

$$E_{\text{rot}} = \sum (2r+1)\epsilon_r\, e^{-\epsilon_r/kT},$$

but $E_{\text{rot}} = \frac{1}{4} \sum_{r\,\text{even}} (2r+1)\epsilon_r\, e^{-\epsilon_r/kT} + \frac{3}{4} \sum_{r\,\text{odd}} (2r+1)\epsilon_r\, e^{-\epsilon_r/kT},$

where the equilibrium ratio at room temperatures and above, ortho/para $= 3:1$, is *frozen in* at low temperatures owing to the infrequent transitions, i.e.

$$C_{\text{rot}} = \tfrac{1}{4}(C_{\text{para}} + 3C_{\text{ortho}}) \text{ per mole,}$$

where

$$C_{\text{para}} = R\sigma^2 \frac{d^2}{d\sigma^2}\ln(1 + 5e^{-6\sigma} + 9e^{-20\sigma} + ...),$$

$$C_{\text{ortho}} = R\sigma^2 \frac{d^2}{d\sigma^2}\ln(3e^{-2\sigma} + 7e^{-12\sigma} + ...).$$

This equation gives excellent agreement with experiment, and can be further checked by working with different mixtures of hydrogen, containing from 100 to 25 per cent. para-hydrogen. In each case the appropriate C_{rot} curve can be followed experimentally. It is interesting to note that for para-rich mixtures C_{rot} passes through a maximum $C_{\text{rot}} > R$.

Before discussing the effect of this 'frozen' equilibrium on the experimental evaluation of the entropy constant of

hydrogen, it is interesting to discuss what causes a transition from the ortho to the para state. At low temperatures the change takes place slowly at high pressures, and with a catalyst of active charcoal the change to the appropriate mixture is complete within half an hour at temperatures of liquid air and liquid hydrogen. By pumping off the equilibrium mixture at the temperature of liquid hydrogen, practically pure para-hydrogen can be obtained, and its properties studied.

The transition ortho $\rightleftharpoons$ para is also catalysed by paramagnetic substances such as oxygen, NO, NO_2, and ions of transitional metals and the rare earth salts. At high temperatures catalysts such as platinum black have an activity in favouring the transition which is parallel with their activity in hydrogenation. Hydrogen atoms also produce the change

$$H_2\,para + H \rightleftharpoons H_2\,ortho + H$$

Spins $\uparrow\downarrow$ $\downarrow$ $\downarrow\downarrow$ $\uparrow$
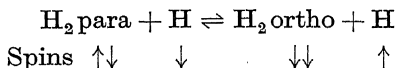
Differences in the physical properties of pure para-hydrogen and the ordinary 25 per cent. mixture are small but definite. Thus the triple point pressure is $53 \cdot 0 \pm 0 \cdot 1$ mm. for para-hydrogen and $53 \cdot 9 \pm 0 \cdot 1$ mm. for the normal mixture.

Entropy constant of hydrogen

The entropy of hydrogen presents certain difficulties of evaluation. either when a purely theoretical method or a purely experimental method is used. The reason is that the theoretical calculation introduces terms for the contribution of nuclear spin to the entropy, which arise in the same form for any change of phase of hydrogen, or for hydrides, but which are not included in any experimental evaluation of $\Delta S = \int C_P\,d \ln T$, since the energy transitions involved would not contribute to C_P till a very low temperature indeed (cf. pp. 59, 72).

In consequence, the theoretical entropy of hydrogen in-

cluding nuclear spin effects (T.N.S. entropy) gives correct values of equilibrium constants and vapour pressures when it is used in conjunction with the T.N.S. entropies of the other substances concerned, but not necessarily when it is used in conjunction with entropies calculated on the basis of the heat theorem and the specific heat integral (H.T. entropy). What happens is that the N.S. contribution cancels when T.N.S. entropies are used consistently, but cannot do so when H.T. entropies are used with T.N.S. entropies in one equation.

A similar problem arises in a modified form whenever the thermodynamic functions calculated on the basis of thermodynamic laws (the H.T. functions) are combined with functions calculated solely from the complete partition function for all forms of energy, these being evaluated from spectroscopic data (the T.N.S. functions). As a general rule the T.N.S. functions include effects which are missed in the H.T. functions, simply because there is no ordinary thermodynamic means of detecting them, i.e. simply because they do not affect the entropy changes in processes such as vaporization or chemical reaction, or changes in heat content (specific-heat determinations). In any particular problem it is always necessary to consider what portions of the T.N.S. function have to be discarded (this merely involves a *change of zero* of the T.N.S. function) before it can be used in conjunction with H.T. functions. Some examples are discussed below.

The H.T. entropy of hydrogen.

Since rotation makes no further contribution to the specific heat of hydrogen at low temperatures it can be treated as a monatomic gas. At rather higher temperatures the contribution of the rotational specific heat to the entropy would be $S_{rot} = \int C_{rot}\, d\ln T$. For example, if the entropy of 'monatomic' para-hydrogen is taken as that of a monatomic gas at low temperatures (cf. p. 31), this would give values of the

entropy of vaporization of solid para-hydrogen (the only experimental check at low temperatures) in agreement with experiment. Furthermore, the rotational specific heat of pure para-hydrogen would give the correct H.T. rotational entropy at somewhat higher temperatures *for any process in which the system contains only para-hydrogen.*

The H.T. entropy of the 3:1 ortho-para mixture at low temperatures does not refer to an equilibrium mixture, and must therefore be used with circumspection. If a process such as vaporization *does not involve any change in the mixture*, the experimentally determined entropy change would agree with the value determined from

$$S_{3:1} = S_{\text{monatomic}} + \int C_{\substack{\text{rot} \\ 3:1}} \, d\ln T.$$

Actually (cf. p. 73) the 3:1 mixture shows a Schottky effect in the solid state which has to be allowed for in calculating the entropy change on vaporization. Thus, neglecting the Schottky effect, the experimental entropy is only 29·65 units at 298° K., in lieu of 31·23.

When the 3:1 mixture takes part in a process at very low temperatures, in which it is changed into the para form, it is doubtful whether thermodynamic functions applying to equilibrium phenomena can be used with advantage. The H.T. entropy is sometimes represented by

$$S_{3:1} = \tfrac{3}{4}S_{\text{ortho}} + \tfrac{1}{4}S_{\text{para}} + \tfrac{3}{4}\ln\tfrac{3}{4} + \tfrac{1}{4}\ln\tfrac{1}{4},$$

the last two are the mixture terms (cf. p. 46), but this expression has practically no connexion with experimental data.

At temperatures between 50° K. and about 300° K. where equipartition has not been completely set up for rotational energy, the correct H.T. function to use for the entropy is

$$S = \tfrac{1}{4}S_{\text{para}} + \tfrac{3}{4}S_{\text{ortho}} + \tfrac{3}{4}\ln\tfrac{3}{4} + \tfrac{1}{4}\ln\tfrac{1}{4},$$

provided there is no change in the 3:1 ratio in the process

whose entropy change is being calculated. This also leads to a cancelling of the mixture terms.

At temperatures above 300° K., $C_{rot} = R$, and hydrogen can be treated as a diatomic gas (at 298° K. the standard entropy is 31·23 units/mole). Applying the standard formula for the entropy constant (p. 37),

$$S = R\left[\ln \mathfrak{A} + \ln \frac{g}{s} + \ln \frac{8\pi^2 I k}{h^2}\right],$$

$$s = 2, \qquad g = 2j + 1 = 1 \quad \text{(p. 115)}.$$

The nuclear spin entropies may be added—using p. 118—but are omitted here, apart from the symmetry factor (p. 120). The entropy constant of the mixture, i.e. of ordinary hydrogen, is thus

$$S = \tfrac{1}{4}S_{para} + \tfrac{3}{4}S_{ortho} + \tfrac{1}{4}\ln\tfrac{1}{4} + \tfrac{3}{4}\ln\tfrac{3}{4}$$

$$= R\left[\ln \mathfrak{A} + \ln \frac{8\pi^2 I k}{h^2}\right] + \ln \tfrac{1}{2} + \tfrac{3}{4}\ln\tfrac{3}{4} + \tfrac{1}{4}\ln\tfrac{1}{4},$$

where the last two 'mixture' terms must be subtracted to give the H.T. entropy (cf. p. 57).

It is useful to note that the chief difficulty in evaluating the entropy of hydrogen arises at temperatures where the 3:1 mixture is not strictly the equilibrium mixture, and that the calculated values can only be used for processes where the ratio ortho/para does not change.

Thermodynamics of deuterium

Two effects have to be discussed in connexion with the thermodynamics of deuterium:

(*a*) A comparison of the rotational heats of H_2, HD, and D_2.

(*b*) A comparison of the chemical constants of H_2, HD, and D_2 and their effect on the position of equilibrium.

The rotational specific heats.

The problem for each gas is to construct the rotational partition function

$$Z_{\text{rot}} = \sum q_r\, e^{-\epsilon_r/kT},$$

since

$$C_{\text{rot}} = R\sigma^2 \frac{d^2 \ln Z_{\text{rot}}}{d\sigma^2}.$$

The nuclei of hydrogen have spin $i = \frac{1}{2}$, of deuterium spin $i = 1$ (in units $h/2\pi$), so that both these gases exist in ortho and para modifications. HD is not a symmetrical molecule, so that rotational transitions from even to odd states are possible. The results can be summarized in a table:

Gas	H_2		HD
Nuclear spin.	$i = \frac{1}{2}$		$i = 1$
Rotational states.	para $r = 0, 2, .$	all values	ortho $r = 0, 2, 4,$
	ortho $r = 1, 3, .$	$r = 0, 1, 2, \ldots$	para $r = 1, 3, 5,$
Quantum wts. of symm./antisymm. eigenfunctions $i/(i+1)$.	$1:3$		$6:3$
Moments of inertia assuming constant separation of atoms.	$0\cdot466 \times 10^{-40}$	$0\cdot62 \times 10^{-40}$	$0\cdot93 \times 10^{-40}$
Minimum quantum change.	$r = 0 \to 2$	$r = 0 \to 1$	$r = 0 \to 2$

It will be noted that for HD the simple partition formula holds (cf. p. 102). This gives a sharp rise in the rotational specific heat in the neighbourhood of Θ_{rot} and a subsequent drop after passing through a maximum, and this behaviour has been experimentally verified.

For D_2 the rotational specific heat of the frozen equilibrium mixture (ortho/para 2:1) is

$$C_{\text{rot}} = \tfrac{2}{3} C_{\text{ortho}} + \tfrac{1}{3} C_{\text{para}},$$

where

$$C_{\text{ortho}} = R\sigma^2 \frac{d^2}{d\sigma^2} \ln \sum_{r\ \text{even}} (2r+1) e^{-\epsilon_r/kT},$$

$$C_{\text{para}} = R\sigma^2 \frac{d^2}{d\sigma^2} \ln \sum_{r\ \text{odd}} (2r+1) e^{-\epsilon_r/kT},$$

and
$$\frac{\epsilon_r \text{ for } D_2}{\epsilon_r \text{ for } H_2} = \frac{I_{H_2}}{I_{D_2}} = \tfrac{1}{2}.$$

The resulting curve is quite different from that for H_2 and has been verified experimentally.[†]

Chemical constants of the gases H_2, *HD, and* D_2.

The equilibrium constant of the reaction
$$H_2O + HD \rightleftharpoons HDO + H_2$$
is 3·8 at 25° C. and 2·0 at 100° C. In general the equilibrium constant in an isotope exchange
$$AH + BD \rightleftharpoons AD + BH,$$
$$K = \frac{[AD][BH]}{[AH][BD]}$$
differs from unity on account of the following factors:
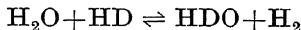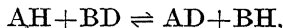
(1) Differences in the zero-point energies of the isotopic compounds. Since $RT \ln K = \Delta F = \Delta H - T\Delta S$, differences in the zero-point energies of e.g. AD and AH will affect $\ln K$ by changing the value of ΔH when hydrogen is substituted for deuterium.

(2) Owing to the different masses of H and D, the entropy constant will differ. The magnitude of the effect will be clear from inspection of p. 36, and is most compactly formulated as follows:
$$S_{D_2} = \tfrac{2}{3}S_{\text{ortho}} + \tfrac{1}{3}S_{\text{para}} + \tfrac{2}{3}\ln 2 + \ln 3 \quad \text{(the mixture terms).}$$
The nuclear spin entropies are omitted apart from the symmetry factor (p. 120), as are the mixture terms.
$$\therefore S_{D_2} = R\left[\ln A + \tfrac{3}{2}\ln M_{D_2} + \ln 8\pi^2 k \cdot_{D_2}\right] + \ln \tfrac{1}{2},$$
where A is a constant,
$$= S_{H_2} + R[\tfrac{5}{2}\ln 2].$$
Similarly, $\qquad S_{HD} = S_{H_2} + R[\tfrac{5}{2}\ln \tfrac{3}{2} - \ln \tfrac{1}{2}].$

From the experimental standpoint, the effect of isotopes

† Clusius and Bartholomé, *Göttinger Nachrichten*, **1** (1934), 1.

on equilibria is readily studied by using hydrogen and deuterium and an exchange catalyst such as platinum. Equilibria in solution may be studied using H_2O and D_2O and acids as exchange catalysts.

A reaction of fundamental importance is

$$H_2 + D_2 \rightleftharpoons 2HD, \qquad K_2 = \frac{[HD]^2}{[H_2][D_2]}.$$
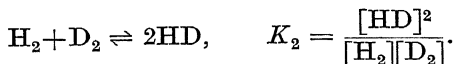
In the region of temperatures where the rotational motion is fully excited, and the vibrational motion is not yet excited, $RT \ln K$

$$= -(2\epsilon_{HD} - \epsilon_{H_2} - \epsilon_{D_2}) + \tfrac{3}{2} \ln \frac{M_{HD}^2}{M_{H_2} M_{D_2}} + \ln \frac{I_{HD}^2}{I_{H_2} I_{D_2}} + \ln 4.$$

The first term on the right-hand side represents the change in zero-point energies, which are

$$\epsilon = hc(\tfrac{1}{2}\nu - \tfrac{1}{4}\nu\chi),$$

where ν is the wave number of the vibrational frequency and χ is the anharmonicity constant. The term $\ln 4$ arises since two symmetrical molecules are changed into two unsymmetrical ones. The experimental result is that

$$2\epsilon_{HD} - \epsilon_{H_2} - \epsilon_{D_2} = \Delta E_0 = -155 \text{ cal./mole}$$

and
$$\ln K_1 = -34/T + 0.6276.$$

The vibrational energy of gases

One of the most general means of determining the specific heat of gases is from the velocity of sound in the gas. After allowing for corrections for departures from the gas laws, usually small under the conditions of experiment,

$$C_P - C_V = R,$$

and the ratio $C_P/C_V = \gamma$ is determined from the velocity

$$u =$$

where P is the pressure and ρ is the density.

After subtracting the translational and rotational specific heats, the vibrational specific heat of the gas can be estimated. For simple diatomic molecules only one mode of vibration is possible, and the partition function for vibrational energy might be expected to be the simple Einstein function (cf. p. 61)

$$Z = \sum_r e^{-h\nu_0(r+\frac{1}{2})/kT},$$

where $\frac{1}{2}h\nu_0$ is the zero-point energy, and the quantum weight is assumed to be unity in the absence of complications.

This result agrees with experiment only for the simplest gases, owing to a number of complications. One of these is that at high frequencies the velocity of sound has been found to vary with the frequency. For carbon dioxide at ordinary temperatures, for example, the velocity begins to increase in the neighbourhood of 10^5 cycles per second and finally reaches a new constant value. This is due to the fact that the vibrational specific heat takes a finite time to come to equilibrium distribution, which may become comparable with the time of an experiment in explosion methods, or for high-frequency sound waves. The vibrations of the molecule then no longer follow temperature changes during the adiabatic pressure changes. Since the velocity of sound is $\alpha\sqrt{\gamma}$ and $\gamma = 1+\dfrac{R}{C_V}$, the decrease in C_V leads to an increase in the velocity of sound.

It should be noted that a modified specific heat might also be more suitable in calculating phenomena such as the velocity of an explosion wave.

A second reason why the simple partition function is unsatisfactory for the vibrational energy is that the individual vibrational quanta are fairly large (compared with rotational quanta, for example), and the vibrations become anharmonic when only a few quanta of energy have been taken up. This means that the value of the nth vibrational level is smaller than $nh\nu_0$, and the values of the separate levels have to be

inserted in the partition function summation. These vibrational levels are deduced from the spectroscopic energy data for the molecule.

The complete partition functions for some simple atoms and molecules.

Apart from the simple theory already discussed, the difficulties in calculating the complete partition functions of even simple molecules are not due to thermodynamics at all but to the complicated nature of band spectra.

The hydrogen atom.

For the *nucleus* of an atom the partition function refers to the number of orientations of the nuclear spin in a perturbing field. At all attainable temperatures the energy of orientation is so small compared with kT that each of the $e^{-\epsilon_r/kT}$ terms in the usual partition function is unity, and $Z_{\mathrm{nucl}} = 2i_s+1$, where i_s is the number of units of nuclear spin $(h/2\pi)$.

The only other energy intake to be considered is the electronic energy. The quantum weight of any electronic energy level is
$$q_{r\,\mathrm{elect}} = (2j_s+1),$$
where
$$j_s = l\pm s \quad (0 \not> j_s),$$
and the electronic partition function is
$$Z_{\mathrm{elect}} = \sum (2j_s+1)e^{-\epsilon j_s/kT}.$$
This function should be summed over all the electronic levels indicated by spectroscopic data, but actually $e^{-\epsilon j_s/kT}$ makes an appreciable contribution to Z only when $T > \epsilon j_s/4k$, so that only the electronic ground state is of importance, except where the separation of electronic energy levels is small.

For *hydrogen* the electronic ground state has quantum number 1 and $j_s = \frac{1}{2}$. The complete partition function (T.N.S.) for the atom is thus
$$Z = Z_{\mathrm{nucl}} \times Z_{\mathrm{elect}} = 2 \times 2 = 4.$$

For *chlorine* $i_s = \frac{5}{2}$ and $Z_{\text{nucl}} = 6$.

The electronic ground state is an inverted doublet ^2P. $j_s = \frac{3}{2}$ for the lower component. For the higher component $\Delta\nu = 881$ cm.$^{-1}$ and $j_s = \frac{1}{2}$. For these two components of the doublet

$$2j_s + 1 = 4 \text{ and } 2 \text{ respectively,}$$

so that

$$Z_{\text{elect}} = 4 + 2e^{-881hc/kT}$$

and the complete partition function is

$$Z = Z_{\text{nucl}} \times Z_{\text{elect}} = 6(4 + 2e^{-881hc/kT}).$$

Quantum weights and degeneracy.

There are several ways of illustrating the origin of the 'multiplicity' of the principal energy levels of atoms and molecules.

From the standpoint of formal wave mechanics, the multiplicity q of a state with energy E arises when there are q distinct proper values satisfying the wave equation of the molecule in the particular quantum state. The proper function of the molecule in this state is then a linear combination of functions with q arbitrary constants. The physical significance of degeneracy may, however, be illustrated in other ways.

The electronic quantum weights for atoms.

The quantum weight of an electronic energy level is $2j_s + 1$, where j_s, the 'inner' quantum number, is the resultant of the magnetic moments due to the spins of the electrons and of the orbital magnetic moments. In vector notation

$$\mathbf{j} = \mathbf{s} + \mathbf{l}.$$

The reason for inserting a quantum weight in statistical theory may be seen by considering what happens in a weak magnetic field. According to the principles of space quantization of magnetic energy, the resultant magnetic axis of the atom will set itself at such angles that its projection along the field can have the series of values

$$m = j, \quad j-1, \quad ..., \quad -1, \quad ..., \quad -j.$$

If the magnetic moment is μm, the energy intake due to these orientations in a field of strength $\mathfrak{H}$ will be obtained from the usual partition function $Z = \sum_m e^{\mu m \mathfrak{H}/kT}$, in which there are $2j+1$ terms. In the absence of the magnetic field $\mathfrak{H} = 0$ and $Z = 2j+1$, which must still be inserted in statistical theory. Multiplicities may thus be regarded as due to the partition of atoms or molecules amongst the minor variations of a given energy level, and must be inserted in order to obtain the correct probabilities in the distribution function.

The rotational degeneracy of diatomic molecules.

A rotational level with energy $E_j = \dfrac{j(j+1)h^2}{8\pi^2 I}$ has the
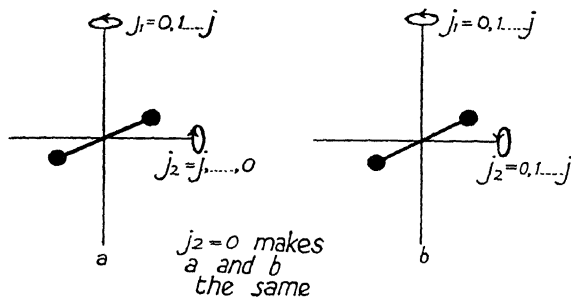
FIG. 11.

multiplicity $(2j+1)$, due to the $(2j+1)$ arbitrary constants in the proper function describing that state.

Another way of illustrating this arises from a consideration of the number of ways in which the j quanta can be partitioned amongst the two rotational axes of the diatomic molecule. The particular arrangements which can be chosen are shown in the diagram. When rotation is taking place about two axes at right angles, a distinction can be made between the case in which the rotation about the second axis is in the same or in the opposite sense. Its physical foundation is clear when the molecule is a dipole, since in

such a case the magnetic axes due to rotation can be distinguished.

There are $j+1$ distributions of the j quanta between the two axes. Each of these, except that for $j_2 = 0$, must be doubled to allow for the sense of the rotations. The total number of minor variations of a rotational level is thus $(2j+1)$.

The complete partition function for some diatomic molecules.

The summation has to be made over every possible electronic, vibrational, or rotational state contributing appreciably to Z. Since the ground electronic state is usually a $^1\Sigma$ term, the multiplicity = 1. Common exceptions are NO, O_2, OH, CN.

It may be noted that cases such as OH and CH are particularly interesting, since reliable estimates of their thermodynamic functions could hardly be obtained except from spectroscopic data. The thermodynamic functions of radicals are of particular value in verifying certain reaction mechanisms in which they are supposed to take part. Complications in applying the theory of the partition functions arise chiefly in the selection of the correct quantum weight for the various states.

Approximate empirical formulae for band spectroscopic frequencies.

When the band spectrum of a molecule has been analysed, the results can usually be expressed in terms of an empirical formula

$$\nu = \nu_0 + \dot{\omega}_e(v+\tfrac{1}{2}) - x\omega_e(v+\tfrac{1}{2})^2 + \ldots +$$
$$+ B_v J(J+1) + D_v J^2(J+1)^2 + E_v J^3(J+1)^3 + \ldots,$$

where

ν_0 is the electronic frequency separation,

ω_e is the fundamental vibration frequency in any electronic state,

x is the anharmonic vibration constant.

The half-quantum of zero-point energy is added to v. v and J

are the vibrational and rotational quantum numbers. B_v and D_v vary with v, i.e.

$$B_v = B_e - \alpha(v + \tfrac{1}{2}) + \gamma(v + \tfrac{1}{2})^2 ...,$$
$$D_v = D_e + \beta(v + \tfrac{1}{2})^2 + \delta(v + \tfrac{1}{2})^4 ... .$$

These formulae allow for changes of moment of inertia in the different rotational levels (the molecule may stretch under the centrifugal force due to rotation) and for the interaction of vibrational and rotational quanta (the average size of the molecule increases with v).

For rigid molecules

$$D_v = E_v = 0, \qquad B_v = \frac{h^2}{8\pi^2 I}.$$

Summation to obtain Z.

Z is determined at a given temperature by summing for all rotational levels, keeping $v = 0$, and repeating for $v = 1, 2, 3,...$ so long as the contribution to Z is still appreciable at the temperature in question. The process is repeated for any electronic levels sufficiently close to the ground state to make an appreciable contribution to Z.

In virtue of the exponential structure of the individual terms in the partition function, when the internal energies (electronic, vibrational, and rotational) can be treated as independent, the complete partition function factorizes into the factors

$$Z = \sum q_{\text{vib}} e^{-\epsilon_{\text{vib}}/kT} \sum q_{\text{rot}} e^{-\epsilon_{\text{rot}}/kT} \sum q_{\text{elect}} e^{-\epsilon_{\text{elect}}/kT}$$
$$= Z_{\text{vib}} Z_{\text{rot}} Z_{\text{elect}},$$

as has already been mentioned (p. 54).

Integration methods can sometimes be used in place of the summation. Thus the simple rotational partition function

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1)e^{-\sigma J(J+1)}, \qquad \sigma = \frac{h^2}{8\pi^2 I k T},$$

can be evaluated by integration at relatively high temperatures where the interval between successive terms is small, giving

$$Z_{\text{rot}} \quad 1/\sigma.$$

It will be noted that this accounts for the rotational entropy term in the entropy constant for simple diatomic molecules (p. 37).

The summation for the complete partition function must then be repeated over a range of temperatures, since the value of Z as a function of temperature is required for a complete evaluation of thermodynamic functions.

Quantum weights in special cases.

In view of the complications arising from the nuclear-spin multiplicity, the quantum weight of rotational states of a molecule is worth special discussion. In general q_r for any state = nuclear spin degeneracy × rotational degeneracy. For a rotational quantum number J, the rotational degeneracy is always $(2J+1)$. The nuclear-spin degeneracy for molecules composed of *dissimilar* atoms is always

$$Z_{\mathrm{nucl}} = (2i_s+1)(2i_{s'}+1),$$

where i_s, $i_{s'}$ are the nuclear spins of the atoms in units $h/2\pi$.

As has already been pointed out, the nuclear-spin degeneracy contributes a term to the T.N.S. functions derived from Z, which is not present in the H.T. functions. It is readily seen that in a reaction

$$AB+CD \rightleftharpoons AC+BD,$$
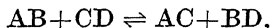
$$Z_{\mathrm{nucl}}\,AB = (2i_A+1)(2i_B+1), \quad Z_{\mathrm{nucl}}\,CD = (2i_C+1)(2i_D+1),$$

$$Z_{\mathrm{nucl}}\,AC = (2i_A+1)(2i_C+1), \quad Z_{\mathrm{nucl}}\,BD = (2i_B+1)(2i_D+1),$$

and

$$\frac{Z_{\mathrm{nucl}}\,AB \; Z_{\mathrm{nucl}}\,CD}{Z_{\mathrm{nucl}}\,BD \; Z_{\mathrm{nucl}}\,AC} = 1,$$

and has no effect on $\Delta F = RT \sum \ln G$, so that for dissimilar molecules the nuclear-spin degeneracy term cancels in any chemical process.

The NO *molecule.*

For diatomic molecules whose ground state is $^1\Sigma$ the rotational partition function is quite straightforward, viz.

$$Z_{\mathrm{rot}} = Z_{\mathrm{nucl}} \sum (2J+1)e^{-\sigma J(J+1)}.$$

When the molecule has more than one electronic state comparable with kT, two further points have to be noted in connexion with rotational quantum weights. Thus NO has two electronic states, $^2\Pi_{\frac{1}{2}}$, $^2\Pi_{\frac{3}{2}}$, separated by only $\Delta\nu \sim 120$ cm.$^{-1}$ The first point is that the smallest value of $J = \frac{1}{2}$ for $^2\Pi_{\frac{1}{2}}$ and $J = \frac{3}{2}$ for $^2\Pi_{\frac{3}{2}}$. The second is that, except for molecules in Σ states, each rotational level is subject to Λ-type doubling into two slightly separated levels whose energy is sufficiently close merely to double the quantum weight $(2J+1)$. Since for oxygen $i_s = 0$ and for nitrogen $i_s = 1$, the nuclear-spin partition function is $1.3 = 3 = Z_{\text{nucl}}$ and the complete rotational partition function allowing for Λ-type doubling is

$$Z_{\text{rot}} = 3.2 \sum_{J=\frac{1}{2},\frac{3}{2},\frac{5}{2}\ldots} (2J+1)e^{\epsilon_J/kT} + 3.2 \sum_{J=\frac{3}{2},\frac{5}{2}} (2J+1)e^{-\epsilon'_J/kT}.$$

Rotational function for diatomic molecules made up of similar atoms.

When the molecule is composed of two similar atoms, the thermodynamic complication may arise, as for ortho- and para-hydrogen at low temperatures, that transitions between odd and even rotational states do not occur. This possibility has already been discussed (cf. p. 102).

When the ground state of the molecule is $^1\Sigma$, the following points have to be regarded when constructing the rotational partition function.

If the nuclei have an even number of units of nuclear spin $(\frac{1}{2}h/2\pi)$ they obey Einstein-Bose statistics, and the nuclear-spin multiplicity of rotational states with J even is $(i_s+1)(2i_s+1)$, and with J odd is $i_s(2i_s+1)$.

An important example is deuterium, which has

$$i_s = 2 \text{ units} = 1,$$

and the rotational partition function

$$Z_{\text{rotD}_2} = 6 \sum_{J \text{ even}} (2J+1)e^{-\sigma J(J+1)} + 3 \sum_{J \text{ odd}} (2J+1)e^{-\sigma J(J+1)}.$$

Hydrogen, on the other hand, has $i_s = 1$ unit, and the nuclear-spin multiplicity of terms with J even is $i_s(2i_s+1)$ and with J odd $(i_s+1)(2i_s+1)$, i.e. the reverse of the above. The rotational partition function for hydrogen is thus

$$Z_{\text{rot H}_2} = 3 \sum_{J \text{ odd}} (2J+1)e^{-\sigma J(J+1)} + \sum_{J \text{ even}} (2J+1)e^{-\sigma J(J+1)}.$$

The molecule $O^{16}O^{16}$.

Since for oxygen $i_s = 0$, the nuclei obey the Einstein-Bose statistics, and the alternate rotational states with J even have nuclear multiplicity 0, i.e. are missing. The ground state of the oxygen molecule is a $^3\Sigma_g^-$ state; the separation of the three energy levels of the triplet is negligible at ordinary temperatures, but the only rotational levels permitted for the three levels of the triplet are

$$F_1: \quad J = \kappa+1, \quad F_2: \quad J = \kappa, \quad F_3: \quad J = \kappa-1,$$

where only odd values of κ are permitted, so that

$$Z_{\text{rot}} = \sum_{\kappa=1,3,5\ldots} (2\kappa+3)e^{-\epsilon_{F_1,J}/kT} + \sum (2\kappa+1)e^{-\epsilon_{F_2,J}/kT} + \sum (2\kappa-1)e^{-\epsilon_{F_3,J}/kT}.$$

The electronic levels of the $O^{16}O^{16}$ molecule proximate to the ground level only begin to affect the complete partition function in the neighbourhood of $1,000°$ K. and $2,500°$ K.

Rotational partition functions at temperatures where $\sigma \ll T$.

When $\sigma \ll T$, the various summations in these partition functions for symmetrical molecules can be replaced by integrations, and since in general

$$\sum_{J=0}^{\infty} (2J+1)e^{-\sigma J(J+1)} = \int_0^{\infty} (2J+1)\, dJ\, e^{-\sigma J(J+1)}$$

$$= \int_0^{\infty} e^{-\sigma x}\, dx = 1/\sigma,$$

where $\quad\quad x = J(J+1),$

it will be seen that for symmetrical diatomic molecules the complete rotational partition function including nuclear-spin multiplicity is

$$Z_{\text{rot}} = \frac{(2i_s+1)^2}{2} \, 1$$

It must be noted that in a reaction where unsymmetrical diatomic molecules are produced from symmetrical molecules, such as

$$\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD} \quad (\text{cf. p. 110}), \qquad \text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB},$$
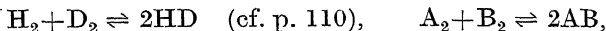
a consideration of the T.N.S. available energies,

$$A_{\text{A}_2} = -RT \ln \frac{(2i_\text{A}+1)^2}{2} \left[\frac{1}{\sigma_{\text{A}_2}} Z_{\text{vib}} Z_{\text{elect}} Z_{\text{trans}} \right]$$

$$= -RT \ln \frac{(2i_\text{A}+1)^2}{2} G'_{\text{A}_2},$$

$$A_{\text{B}_2} = -RT \ln \frac{(2i_\text{B}+1)^2}{2} G'_{\text{B}_2},$$

but $2A_{\text{AB}} = -RT \ln(2i_\text{A}+1)^2(2i_\text{B}+1)^2 G'^2_{\text{AB}}$

and $\Delta A = -RT \ln[2 \times 2] \dfrac{G'^2_{\text{AB}}}{G'_{\text{A}_2} G'_{\text{B}_2}},$

shows that the nuclear-spin multiplicity always cancels, except for the symmetry factor $R \ln 2$ for symmetrical molecules, so that H.T. functions are obtained by omitting the nuclear-spin factors, but retaining the symmetry factor, as was done in the expression for the theoretical chemical constant of diatomic molecules (cf. p. 37).

The only important cases where σ is not small compared with T occur for hydrogen below 273° K. and for deuterium below 200° K., and have already been discussed.

The OH *radical.*

The ground level for the OH radical is an inverted $^2\Pi$ term, i.e. energy of $^2\Pi_{\frac{3}{2}} < {}^2\Pi_{\frac{1}{2}}$. The separation of each of these

into A and B levels is large, so that instead of multiplying each rotational partition function by 2, as for the Λ-type doubling of NO, it is better to take four different partition functions. The nuclear-spin multiplicity is due to $i_s = \frac{1}{2}$ for H and $i_s = 0$ for O, i.e. is 2.

$$Z_{\text{rot}} = 2\left[\sum_{J=0}^{J=\infty}(2J+1)e^{-\epsilon_J/kT}\right] \text{ for all values of } \epsilon_J.$$

Examples for other diatomic molecules could be quoted, but show no special features of interest. For polyatomic molecules the calculation becomes very difficult, since the spectra have by no means been completely resolved. An approximate solution is possible by treating the energy states as independent and the molecules as rigid, so as to separate the partition function into factors. The vibrational partition function is not always easy to evaluate, particularly for long molecules. For smaller molecules it is relatively unimportant, e.g. for N_2O at $298°$ K. $Z_{\text{rot}} = 496$, $Z_{\text{vib}} = 1\cdot1$.

Linear molecules. HCN, N_2O, CO_2, C_2H_2. These are treated as diatomic, and $Z_{\text{rot}} = 1/s\sigma$, where s is the symmetry factor, and integration is permissible since T is large and I is large.

Spherical rotators. CH_4, CCl_4 have $I_A = I_B = I_C$, and when integration is permitted $Z_{\text{rot}} = \sqrt{\pi}/s\sigma^{\frac{3}{2}}$. It may be noted that $s = 12$ for these two molecules. (s is defined as the number of distinguishable permutations produced by rotation of the molecule or its parts.)

Symmetrical top molecules. NH_3, $CHCl_3$, C_2H_6 (double top) have $I_A = I_B \neq I_C$, and when integration is permitted an approximate expression for Z_{rot} is

$$Z_{\text{rot}} = \frac{\sqrt{\pi}}{s\sigma_A\sqrt{\sigma_C}}.$$

For the double top $\quad Z_{\text{rot}} = \dfrac{}{s\sigma_A\sigma_C}$

Asymmetrical top molecules. $I_A \neq I_B \neq I_C$. A convenient approximation for this case is to write

$$I = \sqrt{(I_A I_B I_C)}, \qquad Z_{\text{rot}} = \frac{1}{s} \sqrt{\left(\frac{\pi}{\sigma_A \sigma_B \sigma_C}\right)}.$$

Typical values of s are $H_2O = 2$, $C_6H_6 = 12$.

For more complex molecules the expression

$$Z_{\text{rot}} = \frac{1}{s\pi} \{8\pi^3 (I_A I_B I_C \ldots / h^2)^{1/n}\}^{n/2}$$

has been suggested, but direct experimental verification is difficult.

References to substances whose thermodynamic functions have been evaluated spectroscopically are listed in *Annual Reports Chem. Soc.* **32**, 84 (1936). Amongst the equilibria not easily accessible by other measurements the following may be quoted:

$H_2O = \frac{1}{2}H_2 + OH$.	$N_2 = 2N$.	$NO = N + O$.	$C + 2H_2 = CH_4$.
$2C + 2H_2 = C_2H_4$.	$2C + H_2 = C_2H_2$.	$Br_2 = 2Br$.	$I_2 = 2I$.
$P_2 = 2P$.	$S_2 = 2S$.	$SO = \frac{1}{2}S_2 + \frac{1}{2}O_2$.	
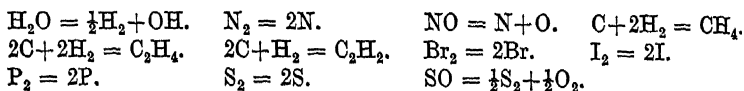
It may be noted that thermodynamic functions calculated spectroscopically agree very well with those evaluated in other ways, with one or two exceptions, such as NO and CO, already mentioned in connexion with the verification of the heat theorem, and with the exception of substances such as ice and ethane, where the discrepancy may be due to incompletely investigated spectroscopic energy levels.

THE THERMODYNAMIC FUNCTIONS OF BLACK-BODY SPACE

IF a cavity is made in a solid body in temperature equilibrium, a small amount of energy will always be present in the cavity even when it is completely freed from matter. This is due to the presence of electromagnetic radiations in the ether. When equilibrium has been reached, the distribution amongst the possible wave-lengths in the ether merely depends on the temperature, and not on the nature of the surrounding bodies. Owing to the fact that a perfectly black body (with emissivity unity for all wave-lengths) would emit radiation with exactly the same energy distribution, the radiation in a cavity in temperature equilibrium with its surroundings is usually called black-body radiation.

Since the energy content of the ether can vary like that of any material substance, its thermodynamic functions can be calculated, not in terms of unit mass, but unit volume. It may be noted that it is desirable to extend the analogy between matter and radiation as far as possible in view of the fact that at very short wave-lengths there is a possibility of the process

$$2h\nu = e_{+} + e_{-}.$$

If E is the energy content in volume V, electromagnetic theory shows that the equation of state of the ether is

$$PV = \tfrac{1}{3}E.$$

The relation between the total energy $\mathfrak{E}$ per unit volume of a black-body enclosure and the temperature may be established by ordinary thermodynamical reasoning.

The entropy change in a reversible isothermal expansion at constant pressure is

$$dS = \frac{d(\mathfrak{E}V + PV)}{T} = \left(\frac{\mathfrak{E} + P}{T}\right) dV + \frac{V}{T}\, d\mathfrak{E}.$$

R 2

Since dS is a perfect differential (cf. p. 3), the R.H.S. must also be a perfect differential, i.e.

$$\frac{\partial}{\partial \mathfrak{E}}\left(\frac{\mathfrak{E}+P}{T}\right) = \frac{\partial}{\partial V}\frac{V}{T} = \frac{1}{T}.$$

Substituting $P = \mathfrak{E}/3$,

$$\frac{d}{d\mathfrak{E}}\left(\frac{4\mathfrak{E}}{3T}\right) = \frac{1}{T},$$

$$-\frac{4\mathfrak{E}}{3T^2}\frac{dT}{d\mathfrak{E}} + \frac{4}{3T} = \frac{1}{T},$$

or

$$\frac{4dT}{T} = \frac{d\mathfrak{E}}{\mathfrak{E}},$$

and

$$\mathfrak{E} = aT^4 \text{ (Stefan's law)},$$

where a is a constant.

The entropy is thus

$$dS = \tfrac{4}{3}aT^3\,dV + 4aVT^2\,dT$$
$$= \tfrac{4}{3}ad(T^3V),$$
$$S = \tfrac{4}{3}aVT^3 + b,$$

where b is a constant.

Distribution of energies among the different wave-lengths in black-body radiation.

This distribution can only be calculated from statistical theory. The problem is how to distribute the total energy $\mathfrak{E}$ amongst the different wave-lengths so as to obtain the most probable distribution.

The number of stationary vibrations in a volume V between wave-lengths λ, $\lambda + d\lambda$ is

$$dZ_\lambda = 8\pi\lambda^{-4}\,d\lambda \times V,\dagger$$

or since $\nu\lambda = c$,

$$dZ_\nu = \frac{8\pi\nu^2}{c^3}\,d\nu \text{ per unit volume.}$$

† This number is twice that on p. 64 to allow for the possible planes of polarization of the electromagnetic waves.

The distribution may be calculated from the Einstein-Bose statistics, or more simply from Planck's original assumption that each of these stationary oscillations of the ether can only be associated with energy

$$\epsilon_\nu = h\nu, \quad 2h\nu, \quad ..., \quad nh\nu, \quad ...,$$

where n is an integer and h is Planck's constant. At temperature T the probability of a vibration of frequency ν with energy $h\nu$, $2h\nu$, and so on, is given by the Boltzmann formula

$$p_{n\nu} = Be^{-nh\nu/kT}.$$

The mean energy of a vibration of frequency ν at temperature T will be obtained from the partition function (cf. p. 61),

$$Z = \sum e^{-nh\nu/kT},$$

$$e_\nu = \frac{h\nu}{e^{h\nu/kT} - 1},$$

and since there are dZ_ν such vibrations the quantity of energy of the black-body radiation contained between ν and $\nu + d\nu$ is

$$E_\nu = \epsilon_\nu dZ_\nu$$

$$\frac{8\pi h\nu^3 \, d\nu}{c^3(e^{h\nu/kT} - 1)}.$$

ADSORPTION EQUILIBRIA

THE adsorption equilibria of gases on solids are worth discussing both because they represent a very characteristic
physico-chemical equilibrium, whose thermodynamical implications are therefore worth attention, and because they
illustrate how equilibrium formulae may be obtained from
the notion of dynamic equilibrium, and the velocities of
sorption and desorption.

The Langmuir adsorption isotherm.

The only case of adsorption to be discussed here is that
of the 'monomolecular layer' of gas held at certain adsorbing
points on the solid, which are assumed to be sufficiently far
apart for the adsorbed molecules to have no influence on one
another, leading to an adsorption potential ϕ independent
of the number of molecules already absorbed.

Dynamic adsorption equilibrium. Equilibrium will be established when the number of molecules evaporating in unit
time equals the number of molecules condensing. If there are
N spaces in all available for adsorption, and the fraction α
is occupied, the number evaporating in unit time will be
given by

$$a\alpha N e^{-E_1/kT},$$

where $e^{-E_1/kT}$ is included to allow for the fact that the molecules must possess energy E_1 above the average before they
can escape, and a is a constant.

The number of molecules condensing will be

$$bp(1-\alpha)N e^{-E_2/kT},$$

since the number approaching the surface in unit time is bp
($b = \sqrt{(1/2\pi mkT)}$, where m is the mass), and the fraction of
the surface uncovered is $(1-\alpha)N$. The term $e^{-E_2/kT}$ is included
to allow for the fact that the molecules may have to possess

some activation energy before they will adhere on collision with an empty space.

Equating the number of molecules condensing with the number evaporating,

$$N a \alpha = b p (1-\alpha) N e^{-(E_2-E_1)/kT} = b p (1-\alpha) N e^{-\phi/kT}.$$

Solving for α,

no. of molecules adsorbed $= N\alpha = N \dfrac{b p e^{-\phi/kT}}{a + b p e^{-\phi/kT}}.$

This formula has the characteristic property that when p is small, the number of molecules adsorbed is proportional to p

$$= N \left(\frac{b}{a} e^{-\phi/kT}\right) p,$$

and when p is large the number adsorbed is

$$N = \text{constant,}$$

i.e. the solid shows the phenomenon of saturation. In actual fact the assumption about non-interference of the adsorbed molecules usually becomes quite unsound long before saturation is reached.

Statistical calculation.

The advantage of a statistical over a dynamical calculation is that the magnitudes of all the constants occurring in the formula are at once determined.

For the distribution of molecules between sorbate and gas, the calculation may be made as follows:

The probability of finding any molecule in the solid sorbate is

$$P_{\text{solid}} = (N_{\text{max}} - N_a) e^{-\phi/kT},$$

where N_{max} is the maximum number of molecules which could be adsorbed, and N_a is the number actually adsorbed, so that $N_{\text{max}} - N_a =$ the number of *available* spaces. The probability of finding it in the gas phase is

$$P_{\text{gas}} = V_{\text{gas}} \frac{(2\pi m k T)^{\frac{3}{2}}}{h^3},$$

so that $\qquad \dfrac{N_a}{N_g} \doteqdot \dfrac{N_{\max} - N_a}{V_g} \dfrac{h^3}{(2\pi mkT)^{\frac{3}{2}}} \varrho^{-\phi/kT}.$

On rewriting this equation it is seen to give the same ɪ as before, namely, since $V_g/N_g = kT/p$,

$$N_a = \frac{N_{\max} e^{-\phi/kT} bp}{1 + bpe^{-\phi/kT}}$$

where $\qquad b = \dfrac{h^3}{(2\pi mkT)^{\frac{3}{2}}} \dfrac{1}{kT}.$

The comparison just made between the statistical dynamical methods of calculating equilibrium illustrates general features of the dynamical method of calculaʈ any equilibrium. When the phenomena occurring are fɑ simple, the correct dependence of the equilibrium on pressɪ etc., is obtainable without difficulty and with much simɪ theoretical foundations than in the statistical method. is usually necessary to leave the velocity constants undeɪ mined, however.

The statistical method, on the other hand, not only deɪ mines the dependence of equilibrium on pressure, etc., ɪ also gives the *ratio* of the velocity constants of the proces in dynamic equilibrium. It is from this property that extɪ sions of thermodynamic theory to the velocity of reactiɑ are being developed.

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